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ORGANIC CHEMISTRY

FOR ADVANCED STUDENTS

BY

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PREFACE

THE present volume is an enlarged edition of that published in 1887, and has been completely rewritten. The preparations have all been carefully revised, some of the former ones omitted and many new ones introduced. The chief additions are the introductory chapters on organic analysis and molecular weight determinations, and an extension of the appendix.

The book does not aim at being a complete laboratory guide, but is intended to provide a systematic course of practical instruction, illustrating a great variety of reactions and processes with a very moderate outlay in materials and apparatus.

The objection may be raised that the detailed description of processes makes no demand upon a student's resourcefulness or ingenuity. It must be remembered, however, that the manipulative part of organic chemistry is so unfamiliar to the elementary student that he requires minute directions in order to avoid waste of time and material. Until he has acquired considerable practical skill he cannot accomplish the experimental work requisite for research, and repeated failures will be apt to destroy his confidence in himself.

To satisfy, to a legitimate extent, the prejudices of certain examining bodies, who still adhere to the old system of testing a student's knowledge of practical organic chemistry by means of the qualitative analysis of certain meaningless mixtures, the special tests for some of the more common organic substances have been inserted. At the same time, an attempt has been made at the end of the appendix to systematise the analysis of

organic substances on a broader and therefore more rational basis.

The present occasion seems opportune to direct attention to the fact that one of the most familiar, most readily procurable and most cheaply produced of all organic materials is placed beyond the reach of many students by the heavy duty levied upon it. May I, in the name of teachers of organic chemistry, appeal to the Board of Inland Revenue, on behalf of scientific and technical education, to provide institutions for higher education in science with a limited quantity of pure alcohol free of duty, thereby placing schools of chemistry in this country in the same position as those on the Continent?

In conclusion I desire to thank Dr. J. McCrae, who has written the section on Ethyl Tartrate and the use of the Polari-meter, Dr. T. S. Patterson, who has been kind enough to look over the proofs, and Mr. H. D. Dakin, who has given me sub-stantial assistance in the practical work of revision.

<div style="text-align: right">J. B. COHEN.</div>

THE YORKSHIRE COLLEGE,
    October, 1900.

·CONTENTS

ORGANIC ANALYSIS

Estimation of Carbon and Hydrogen

Qualitative Examination. — Carbon compounds are frequently inflammable, and when heated on platinum foil take fire or char and burn away. A safer test is to heat the substance with some easily reducible metallic oxide, the oxygen of which forms carbon dioxide with the carbon present. Take a piece of soft glass tube about 13 cm. (5 in.) long, and fuse it together at one end. Heat a gram or two of fine copper oxide in a porcelain crucible for a few minutes to drive off the moisture, and let it cool in a desiccator. Mix it with about one-tenth of its bulk of powdered sugar in a mortar. Pour the mixture into the tube, the open end of which is now drawn out and bent at the same time into the form shown in Fig. 1. This is done by shaking down the mixture

FIG. 1.

to the closed end and revolving the tube in the blow-pipe flame about 2½ cm. (1 in.) beyond the mixture, until it is thoroughly softened. The tube is then removed from the flame, drawn out gently and bent. Make a file scratch across the end of the capillary and break it. When the tube is cold tap it horizontally at the edge of the bench, so as to form a free channel above the mixture. Suspend it by a copper wire to the ring of a retort stand, and let the open end dip into lime or baryta water. Heat the mixture gently with a small flame. The

B

gas which bubbles through the lime water turns it milky. Moisture will also appear on the sides of the tube, which, provided that the copper oxide has been thoroughly dried beforehand, indicates the presence of hydrogen in the com-

FIG. 2.

pound. Gases, or volatile substances like ether and alcohol, cannot, of course, be examined in this way ; but an apparatus must be arranged so that the gas or vapour is made to pass over a layer of red hot copper oxide and then through the lime water.

Quantitative Estimation.—The principle of the method is that just described under *qualitative examination*, but the substance and the products of combustion, viz., carbon dioxide and water, are weighed. The following apparatus is required.

1. *An Erlenmeyer or other form of Combustion Furnace.*—The usual length is 80-90 cm. (31-35 in.), and it is provided with 30 to 35 burners. Flat flame burners are undesirable.

2. *A Drying Apparatus.*—A form of drying apparatus which is easily fitted together is shown in Fig. 2. It consists of four large U-tubes arranged side by side in pairs. The U-tubes are mounted upon a wooden stand with two uprights, to which the two pairs of tubes are wired. The first of each pair is filled with soda-lime, and the second with pumice soaked in concentrated sulphuric acid. Each soda-lime tube is connected with a sulphuric acid tube by well-fitting rubber corks and a bent glass tube. The two other limbs of the sulphuric acid U-tubes are joined by a three-way tap forming a T-piece. The free end of the T-piece is attached to a small bulb tube, Fig. 3, containing a drop of concentrated sulphuric acid to mark the rate

FIG. 3.

at which the bubbles are passing through the drying apparatus. The bulb tube is connected with the combustion tube by a short piece of rubber tubing and a short glass tube, which passes through a rubber cork fixed in the end of the combustion tube. The rubber tubing carries a screw-clip. The open ends of

the soda-lime U-tubes are closed with rubber corks, through which pass bent glass tubes. One of these glass tubes is connected by rubber tubing to an oxygen gas-holder or to a cylinder of compressed oxygen, which must be furnished with an automatic regulating valve, and the other glass tube is attached to a gas-holder containing air. By turning the three-way tap, either oxygen or air may be supplied to the combustion tube.

3. *A Combustion Tube of Hard Glass.*—It should be about 13 mm. inside diameter, and the walls not more than 1·5 mm. thick. Its length should be such that it projects at least 5 cm. (2 in.) beyond the furnace at either end. After cutting the required length, the ends of the tube are carefully heated in the flame until the sharp edges are just rounded. The tube is filled as follows. Push in a loose asbestos plug about 5 cm. (2 in.) from

FIG. 4.

one end. This end, to which the calcium chloride tube and potash apparatus are subsequently attached, may be called the *front end*. Pour in coarse copper oxide at the opposite end and shake it down to the plug until there is a layer about two-thirds the length of the tube. Keep the oxide in position by another plug of asbestos ; see that the plugs are not rammed too tight. Make a roll of copper gauze about 13 cm. (5 in.) long to slide easily into the back end of the combustion tube. This is done by rolling the gauze tightly round a stout copper wire until the requisite thickness is obtained. The projecting ends of the wire are then bent over into hooks as shown in Fig. 4. This roll, or spiral, as it is usually called, is subsequently oxidised. It is pushed into the tube or withdrawn as occasion requires by a piece of hooked wire. The combustion tube is placed on a layer of asbestos in the iron trough of the furnace. The arrangement of the tube with boat and spiral is shown in Fig. 5.

4. *A Straight Calcium Chloride Tube.*—It is inserted through a rubber cork and fixed in the front end of the combustion tube when the latter is not in use, as copper oxide is very hygroscopic, and it is necessary to protect it from the moisture in the air.

5. *A Potash Apparatus.*—Several forms of potash apparatus
are made ; that of Geissler (Fig. 6), and Classen (Fig. 7) being
perhaps most commonly employed.   The latter has the advan-
tage of being very light.   The removable side tube is filled
with granulated calcium chloride or soda-lime, with a plug of
cotton wool at each end.   The bulbs of the apparatus are filled

FIG. 5

with a strong solution of caustic potash containing 25 grams of
potash to 50 c.c. of water.   This is done as follows.   Remove
the soda-lime tube and attach in its place a piece of rubber
tubing.   This serves as a mouthpiece.   Pour the potash
solution into a basin and dip the other end of the potash
apparatus under the liquid.   Suck at the rubber tube until the
quantity appears sufficient to fill the bulbs.   Remove the
potash solution and continue to suck until the solution is trans-
ferred to the bulbs.   The bulbs should be nearly filled.   In the
case of Classen's apparatus, the liquid should stand half an inch
deep in the bottom of the apparatus outside the lowest bulb.
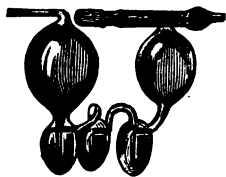
FIG. 6

FIG. 7.

Wipe the potash solution from the outside and inside of the
inlet tube of the apparatus with filter paper.   Smear a thin film
of vaseline on the ground end of the soda-lime tube before
replacing it, and fit to the open ends of the apparatus, stoppers
of rubber and glass rod, which are not removed, except when
the apparatus is in use.   As the potash apparatus has to be

refilled after every two combustions, it is advisable to keep a little stock of solution in a bottle fitted with an ordinary cork.

6. *A Calcium Chloride* ⋃-*Tube.*—The form of calcium chloride tube is shown in Fig. 8. It is fitted with sieved calcium chloride to within $2\frac{1}{2}$ cm. (1 in.) of the side pieces, and then with coarser pieces to within $\frac{1}{2}$ cm. ($\frac{1}{4}$ in.). Place a small plug of cotton wool in both limbs above the chloride to keep it in position. Two well-fitting corks, cut off level with the glass and coated with sealing-wax, pro- duce an effective air-tight stopper to the open limbs, but it is preferable to seal

FIG. 8.

them in the blow-pipe flame. The sealing requires a little skill. Carefully wipe off any chloride dust which may have adhered to the open ends of the two limbs. Cork up one limb and stopper one of the side tubes. Attach a short piece of rubber tubing to the other side tube to serve as a mouthpiece. Now soften the end of the open limb in a small blow-pipe flame, and at the same time heat the end of a short piece of glass rod. With the hot end of the rod gather up the edges of the open limb, and whilst rotating the limb backwards and forwards in the flame, draw it out and seal it up. If successful, the appear- ance of the tube is that shown in Fig. 9. The blob of glass is heated in a small flame, and, by gently blowing and re-heating
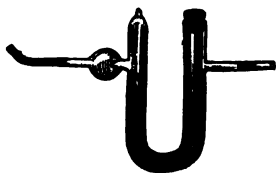
FIG. 9.

and blowing again, the blob can be removed, and, finally, by using a rather larger flame, heating and blowing alternately, the end is neatly rounded.

7. *A Porcelain or, preferably, a Platinum Boat.*—See that it slips easily into the combustion tubes. The boat is kept in a desiccator on a flat cork or support made of glass rod when not in use.

Preparation of the Tube.—Before starting the com- bustion it is necessary to clean and dry the combustion tube. This is effected by heating the whole length of the tube con- taining the copper oxide and spiral gradually to a dull red heat, and passing through it a slow stream of dry oxygen from the

gas-holder or cylinder.   As soon as a glowing chip is ignited at
the front end and the moisture, which at first collects there, has
disappeared, the gas jets are turned down and finally ex-
tinguished.   The oxygen is then stopped, and the straight
calcium chloride tube inserted into the open end of the tube.

Preliminary Operations.—Grind up a little pure oxalic
acid, and carefully weigh out ·15 to ·2 gram (not more) in the
boat.   Weigh also the calcium chloride tube and potash appa-
ratus without stoppers or other accessories.   The side tube of
the calcium chloride tube, which carries the bulb, is attached
directly to the combustion tube with a rubber cork.   This cork
should be carefully selected, and should exactly fit the com-
bustion tube.   The bore hole should be small and smooth, and
it is advisable to dust it with graphite or coat it with a film of
vaseline to prevent the rubber from clinging to the glass, a
matter of frequent occurrence unless this precaution is taken.
The cork should be kept exclusively for the combustion.   Push
the side tube of the calcium chloride tube through the hole until
it is flush with the opposite surface, and squeeze the cork tightly
into the combustion tube.   Attach the potash apparatus to the
other limb of the calcium chloride tube by a well-fitting piece
of rubber tubing about 3 cm. (1½ in.) long, and bring the ends
of the glass as closely as possible together.   It should be
unnecessary to wind wire round the joint if the rubber is of the
right diameter.   A little vaseline may be used here with advan-
tage, but only in the thinnest film.   The potash apparatus
will require to be supported upon a block or stand.   Remove
the copper spiral from the back of the tube.   Introduce the
boat and push it into position against the asbestos plug by
means of the spiral which is placed behind it.   Replace the
rubber cork connected with the drying apparatus.   The apparatus
will present the appearance shown in Fig. 10.

It must now be tested to see that it is air-tight.   For this
purpose, close the open end of the potash apparatus with a
tight stopper and turn on the full pressure from either gas-
holder.   After the first few bubbles of air have passed through
the bulbs of the potash apparatus no further movement of
bubbles should appear *in any part* of the apparatus.   If it
withstands this test, the combustion may proceed.   Release the
pressure by closing the tap of the gas-holder, screwing up the

clip at the back of the combustion tube, and cautiously removing the stopper from the potash apparatus. Then raise the three-way tap from its socket for a moment.

The Combustion.—Turn on the oxygen and adjust the rate of flow through the apparatus by means of the screw-clip so that 2 or 3 bubbles per second pass through the potash bulbs. Throw back the tiles if closed, and light the burners under the front layer of copper oxide to within 10 cm. (4 in.) of the boat and also 2 or 3 burners under the spiral behind the boat, but not within 5 cm. (2 in.) of the boat. Turn up the gas slowly to avoid cracking the tube and in a minute or two, when the tube is thoroughly warmed, close the tiles over the lighted burners and heat to a dull red heat. A vivid red heat during the combustion is not only unnecessary, but undesirable, as the glass is apt to soften and be distorted and even to blow out and

FIG. 10.

become perforated. A combustion tube carefully handled should last indefinitely. When the copper oxide is red hot, turn on the burners very gradually from the spiral towards the boat, but do not close the two pairs of tiles over the boat until the combustion is nearly terminated and the burners are all lighted. The first indication of the substance burning is the appearance of a film of moisture at the front end of the combustion tube and an increase in the speed of the bubbles passing through the potash apparatus. The front end of the tube, which should project 4 to 5 cm. ($1\frac{1}{2}$ to 2 in.) from the furnace, must be kept sufficiently hot to prevent moisture permanently condensing there ; but it must never be allowed to become so hot that there is any risk of the cork being burnt, and it should always be possible to place the finger and thumb round the part of the tube where the cork is inserted. A screen made from a square piece of asbestos board, with a slit in it

slipped over the tube at the end of the furnace, may be used with advantage.

The speed of the bubbles is the best indication of the progress of the combustion. If the rate increases so that the bubbles passing through the last bulb cannot easily be counted, a burner or burners must be lowered or extinguished until the speed slackens. After a time, when the air has been displaced and carbon dioxide largely fills the tube, the gas is nearly all absorbed in the first potash bulb. When this occurs, the current of oxygen may be increased until the bubbles appear synchronously in the bulbs, when the current is again checked. If some copper oxide has been reduced in the first stages of the process, the bubbles in the potash apparatus may entirely cease for a time, but will reappear when the copper has been reoxidised. Here again an increased current of oxygen will hasten the process. The combustion is complete when a glowing chip held at the end of the potash apparatus is rekindled. All the moisture must by now have been driven over into the calcium chloride tube. If this is not the case, warm the end of the tube cautiously with a small flame, or by means of a hot tile held near the tube   The time required to complete the combustion is about one-half to three-quarters of an hour from the time the front of the tube is red hot, but more volatile substances, which must be heated more cautiously, will naturally take longer.

The combustion being complete, gradually turn down, and in a few minutes extinguish, the burners. Whilst the furnace cools the oxygen is replaced by a slow current of air. To do this the oxygen supply is stopped and the three-way tap is turned through 180°, so as to connect the tube with the air reservoir, the tap of which is then opened and the stream of air regulated by the screw clip.

Let the air pass through for 20 minutes whilst the furnace is cooling down. Then remove and stopper the potash apparatus and the calcium chloride tube, and after allowing them to stand by the balance case for half-an-hour, weigh.

The results are calculated in percentages of carbon and hydrogen as follows :

w is the weight of substance taken.
a is the increase in weight of the potash apparatus.

b is the increase in weight of the calcium chloride tube.

$$\frac{12 \times a \times 100}{44 \times w} = \text{per cent. of carbon.}$$

$$\frac{2 \times b \times 100}{18 \times w} = \text{per cent. of hydrogen.}$$

Example—·1510 gram of oxalic acid gave ·1055 gram of CO_2 and ·068 gram of H_2O.

$$\frac{12 \times ·1055 \times 100}{44 \times ·1510} = 19·05 \text{ per cent. of carbon.}$$

$$\frac{2 \times ·068 \times 100}{18 \times ·1510} = 5·00 \text{ per cent. of hydrogen.}$$

Calculated for $C_2H_6O_6$: C = 19·04 per cent. ; H = 4·76 per cent.

As a rule, the carbon is a little too low through loss of moisture from the potash apparatus, whilst the hydrogen is too high, probably through incomplete drying of the air and oxygen from the gas-holders. The discrepancy should not exceed ·2 per cent. of the theoretical amount. If the substance burns with difficulty it should be mixed with fine copper oxide in the manner described under quantitative estimation of nitrogen.

The Combustion of Volatile and Hygroscopic Substances.—If the substance is a non-volatile liquid it may be weighed in a boat like a solid ; if it is hygroscopic the boat must be enclosed and weighed in a stoppered tube. If it is a volatile liquid a glass bulb or tube, drawn out into a neck as shown in Fig. 11, must be used. The bulb is first weighed, and the liquid is introduced by warming the bulb gently to expand the air and then inverting the open neck under the

FIG 11.

liquid. The operation may require repeating. The tube is then sealed and weighed again. Before introducing the bulb into the tube the neck is nicked with a file and broken off. It is then placed in the boat and pushed into the combustion tube. In the combustion of a substance like naphthalene, which is moderately volatile, the greater part is vaporised by the heat of the copper oxide spiral in contact with the boat. The

burners are therefore not lighted under the boat until towards the close of the combustion. In the case of a highly volatile compound like ether, a combustion tube is used, which projects at least 15 cm. (6 in.) beyond the back of the furnace. The bulb containing the substance is then placed just outside the furnace, and then the spiral in contact with it. A small Bunsen flame is placed under the end of the spiral away from the substance, the heat from which is sufficient to completely volatilise the substance at a convenient speed.

The Combustion of Organic Substances containing Nitrogen.—The following modification must be introduced in cases where the organic substances contain nitrogen. As the nitrogen may be liberated in the form of one or other of its oxides, which are liable to be absorbed in the potash apparatus, a source of error is introduced, which may be eliminated in the following way. A spiral of metallic copper is brought into the front end of the combustion tube, which, when red hot, reduces the oxides of nitrogen. The free nitrogen then passes through unabsorbed. About 13 to 15 cm. (5 to 6 in.) of coarse copper oxide is removed from the front end of the tube, and after inserting an asbestos plug, the space left by the oxide is filled with a roll of copper gauze 13 to 15 cm. (5 to 6 in.) long. The copper spiral must have a clean metallic surface, which is easily produced in the following way. Take a large test-tube or boiling tube, an inch or so longer than the spiral, and push down to the bottom a small pad of asbestos. Pour in about 5 c.c. of pure methyl alcohol.

Have a cork at hand which fits loosely into the mouth of the test-tube. Wrap the tube round with a duster. Hold the copper spiral with the crucible tongs in a large blow-pipe flame until it is red hot throughout and slide it quickly into the test-tube. The methyl alcohol reduces the film of oxide on the copper and is at the same time oxidised to form aldehyde, the vapours of which attack the eyes if the tube is brought too near the face. The alcohol takes fire at the mouth of the test-tube. When the flame dies down insert the loose cork and let the tube cool. The spiral, which has now a bright surface, is withdrawn, and the excess of alcohol removed by shaking it. It must now be thoroughly dried. Place the spiral in a hard glass tube a few inches longer than the spiral and fitted at each end with a cork,

into which short, narrow glass tubes are inserted. Attach one end of the tube to an apparatus for evolving carbon dioxide, which is thoroughly dried by passing it through concentrated sulphuric acid. When the air is expelled from the tube, heat it gently until the alcohol is removed. Then let the tube cool while the gas is passing through. The spiral is then removed and placed in the front of the combustion tube. The combustion is carried out in the manner already described, but a current of air is substituted for oxygen until all the hydrogen has been expelled, *i.e.*, until water ceases to condense in the front of the tube. The burners under the metallic copper are then gradually extinguished, and the spiral allowed to cool whilst the current of air is replaced by oxygen. By the time the oxygen reaches the spiral, the latter should have so far cooled that it remains unoxidised. The current of oxygen is continued until a glowing chip is kindled at the end of the potash apparatus and the operation is completed by turning on the air as previously described.

A convenient substance to use for analysis is acetanilide, see Preparation 49, p. 131.

Combustion of Organic Compounds containing Halogens and Sulphur.—When the halogens or sulphur are present in an organic compound, they are liable to be absorbed either in the free state or in combination with oxygen in the potash apparatus. In this case, fused lead chromate broken up into small pieces must replace the coarse copper oxide in the combustion tube. The halogens and sulphur are retained by the lead, the former as the halide salt, and the latter as lead sulphate. Special care must be taken in using lead chromate, that the temperature of the furnace is not too high, as otherwise the chromate fuses to the glass, and the combustion tube then cracks on cooling.

Estimation of Nitrogen.

Qualitative Examination.—When nitrogenous organic compounds are heated with metallic potassium or sodium, potassium or sodium cyanide is formed, and the subsequent test is the same as for a cyanide. Pour about 10 c.c. of distilled water into a small beaker. Put a fragment of gelatine or cheese into a small test-tube along with a piece of metallic potassium

or sodium the size of a coffee bean, and heat them at first gently until the reaction subsides, and then strongly until the glass is nearly red-hot. Then place the hot end of the tube in the small beaker of water. The glass crumbles away, and any residual potassium is decomposed with a bright flash, all the cyanide rapidly goes into solution, whilst a quantity of carbon remains suspended in the liquid. Filter through a small filter into a test-tube. Add to the clear solution about 1 c.c. of ferrous sulphate solution, to which a drop of ferric chloride has been added, boil up for a minute, cool, and acidify with dilute hydrochloric acid. A precipitate of Prussian blue indicates the presence of nitrogen. If the liquid has a blue colour, let it stand for an hour and examine it again for a precipitate. If no precipitate appears and the solution remains of a clear, yellowish-green colour, no nitrogen is present.
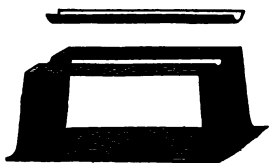
FIG. 12.

Quantitative Estimation (Dumas). — According to this method, a weighed quantity of the substance is heated with copper oxide in a tube filled with carbon dioxide. The carbon and hydrogen form respectively carbon dioxide and water, and the nitrogen which is liberated in the form of gas is collected over caustic potash (which absorbs the carbon dioxide) and measured.

The following apparatus is required :—

1. *A combustion furnace* of the ordinary form.

2. *A short furnace* of simple construction, such as used in Turner's method for estimating carbon in steel (Fig. 12). It should carry an iron trough about 30 cm. (12 in.) long, fixed at such a height that it can be heated by an ordinary Bunsen burner.

3. *A combustion tube*, which may be rather longer than that used in the estimation of carbon and hydrogen.

4. *A short hard glass tube*, 25—28 cm. (10—11 in.) long, and closed at one end.

5. *A bent tube with a bulb*, blown in the centre, as shown at *a*, Fig. 13. This is attached by rubber corks to the ends of the long and short combustion tubes.

6. *A graduated Schiff's Azotometer*, Fig. 13.—A small quan-

tity of mercury is first poured into the bottom of the tube so as
to fill it 4—5 mm. above the lower side limb.   A solution of
potash (1KOH : 3H$_2$O) is then poured into the glass reservoir,
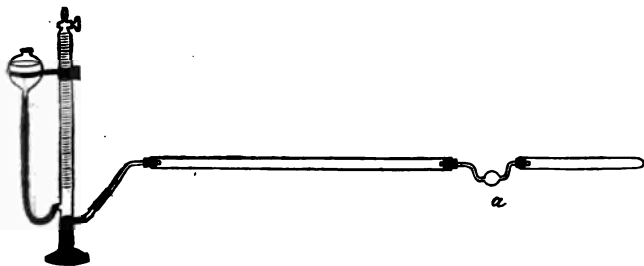
FIG. 13

which is attached to the upper straight side limb by a rubber
tube.   By raising the reservoir and opening the tap the tube is
filled, and remains so on closing the tap and lowering the reser-
voir.   When the tube is filled with potash solution there should
be sufficient mercury at the bottom to seal off the potash solu-
tion from the bent limb, which connects with the combustion
tube.

7. *Two flasks,* 200 *c.c.* and 300 *c.c.*—The necks are slightly
constricted in the blow-pipe flame, so that the
end of the combustion tube slips in as far as
the constriction (Fig. 14).   The flasks are fitted
with good corks.

8. *A spiral of copper gauze* 15 cm. (6 in.)
long, which is reduced in methyl alcohol as
described on p. 10.   The spiral should be re-
duced just before use when the tube is filled
and ready.   It is unnecessary to remove all the
alcohol from the spiral by heating it in a
current of carbon dioxide.   It is sufficient to
whisk it sharply through the air and shake off
the excess of liquid.

FIG. 14.

9. *A sufficient quantity of coarse copper oxide*
to fill the combustion tube two-thirds full and a further quantity
of fine copper oxide to occupy 10—13 cm. (4—5 in.) of the tube.

10. *Two shallow tin dishes*, 10—13 cm. (4—5 in.) in diameter for roasting copper oxide. These dishes can be obtained from the ironmonger in different sizes and are useful in the laboratory for a variety of purposes, such as for oil, metal or sand-baths.

11. *A square of copper gauze* of moderate mesh of the area of the tin dish. It is turned up at the edges and is used for sifting the coarse from the fine copper oxide after each combustion.

12. *Pure sodium bicarbonate*, $NaHCO_3$, in powder free from ammonia.

Filling the Combustion Tube.—A plug of asbestos is first pushed in from one end far enough to leave room for the copper spiral, which should lie well within the furnace. This end of the tube is subsequently attached to the azotometer and may be called the *front* end. The coarse copper oxide is heated over a Bunsen burner in one of the shallow tin dishes and the fine oxide in another. After about a quarter to half an hour the burners are extinguished and the oxides whilst still warm are introduced into their respective flasks with drawn-out necks. The flasks are closed with corks and allowed to cool. The back end of the combustion tube is now pushed horizontally into the neck of the coarse oxide flask and the oxide poured on to the plug by tilting the flask and tube. The tube is filled with oxide about two-thirds of its length. Into the flask containing the fine oxide about ·2 gram of powdered substance (acetanilide may be conveniently used, see Prep. 49 p. 131) is weighed out by difference from a sample tube, which should contain the approximate quantity. The substance is then well mixed with the oxide by shaking the flask. The contents of the flask are carefully poured into the tube above the coarse oxide in the manner described and the flask is rinsed out with coarse oxide, which is likewise poured into the tube until it is filled to the full length of the furnace. A loose plug of asbestos is pushed in to keep the materials in position and the tube is tapped horizontally on the bench in order to form a channel above the layer of fine copper oxide. The tube is now laid in the furnace, which is tilted a little forwards in order to collect the moisture at the front end of the tube. The short closed tube is well packed with powdered sodium bicarbonate and tapped horizontally so as to form a good channel above the whole

length of the substance. It is laid in the small furnace, which is also tilted forwards to drain off the water which is formed. The bicarbonate and the combustion tubes are connected by the bulb tube already described. The copper spiral is now reduced and pushed into the front of the tube up to the plug and finally the azotometer is attached by its bent tube. The arrangement of the tubes and their contents are shown in Figs. 13 and 15.

The Combustion.—The tap of the azotometer is opened and the reservoir lowered so as to empty as far as possible the graduated tube. The joints of the apparatus being well secured, begin by cautiously heating the bicarbonate near the closed end of the tube with a good burner, and concentrate the heat by tiles placed on each side. A rapid stream of carbon dioxide is at once evolved. When it begins to slacken, push the
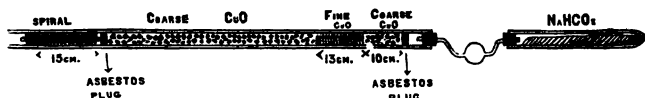
FIG. 15.

burner on ½ cm. or so in order to maintain a continuous and rapid stream. The quicker the stream of gas, the sooner is the air expelled, for the gas then pushes the column of air before it like a piston, before the latter has time to diffuse. In about ten minutes, the row of burners beneath the spiral and the coarse oxide to within 10 cm. (4 in.) of the fine oxide may be lighted. In another fifteen minutes, the gas which is passing through the tube may be tested. The current is allowed to slow down a little, and the graduated tube of the azotometer is then filled with potash solution by raising the reservoir and closing the tap. On gradually lowering the reservoir, a few bubbles will pass up the graduated tube.

By the time they reach the top of the tube, the size of the bubbles should have become so minute that when collected at the top they occupy no appreciable volume, but appear as a fine froth. If this is not the case, open the tap, run out the solution and continue as before to drive carbon dioxide through the tube. Repeat the test in another five minutes. Not more than half the bicarbonate should have been utilised in expelling the air.

The air being removed, the combustion of the substance is commenced. The azotometer is filled with the potash solution, the tap closed, and the reservoir lowered as far as possible. The current of carbon dioxide is allowed to slacken, but it must not be completely stopped. The front portion of the combustion tube will by this time have reached a dull red heat. A few more burners are now lighted on both sides of the fine oxide. Finally, the layer of fine oxide is gradually heated and the process conducted in much the same manner as that described under the estimation of carbon and hydrogen. The combustion is regulated by the speed of the bubbles passing up the azotometer tube, which should enable them to be readily counted. The burners being all lighted and the tube red hot throughout, the tiles above the substance are closed. The current of gas will shortly slacken. The residual nitrogen is then expelled from the tube by moving on the flame beneath the bicarbonate and causing a fresh stream of carbon dioxide to sweep through the tube. Care must be taken that the stream of gas is not too rapid, as otherwise the potash solution may become saturated and driven completely into the reservoir. The burners may now be extinguished and a reading of the level in the azotometer taken every few minutes until it remains constant and the bubbles are completely absorbed. Remove the azotometer by slipping out the cork from the front of the combustion tube, and hang a thermometer beside it. Do not, however, stop the flow of carbon dioxide until the tube is nearly cold. In this way, the copper spiral remains quite bright and may be used for a second determination without being reduced.

When the azotometer has stood for an hour in a cool place, adjust the level by raising the reservoir so that the liquid in the tube and reservoir stand at the same height. Read off the volume, and at the same time note the temperature and the barometric pressure.

The percentage of nitrogen may be calculated as follows :—

v is the observed volume of nitrogen.

B is the height of the barometer in mm.

t is the temperature.

f is the vapour tension of the potash solution, which may be taken to be equal to that of water without serious error.

The volume corrected to 0° and 760 mm. will be given by the following expression :—

$$\frac{v \times 273 \times (B-f)}{(273 + t)\, 760}.$$

As the weight of 1 c.c. of nitrogen at 0° and 760 mm. is ·00126 gram, the percentage weight of nitrogen will be given by the expression

$$\frac{v \times 273 \times (B-f)}{(273 + t)\, 760} \times \frac{·00126 \times 100}{w},$$

where w is the weight of substance taken.

Example—·206 gram of acetanilide gave 18·8 c.c. of moist N at 17° and 756 mm. [f at 17° = 14·5 mm.]

$$\frac{18·8 \times 273 \times (756 - 14·5) \times ·126}{(273 + 17) \times 760 \times ·206} = 10·56 \text{ per cent.}$$

Calculated for C_8H_9ON ; N = 10·37 per cent.

Instead of collecting the gas over dilute potash solution, it is often customary to use a very strong solution consisting of equal weights of potash and water. The vapour tension is practically *nil*. Or, again, the nitrogen may be transferred to a graduated tube standing over water, which gives a result free from any error arising from incorrect vapour tension. The manner of transferring the gas is shown in Fig. 16. The stem of a wide funnel is cut off and attached by rubber to the top of the azotometer. This is then filled with water and the projecting end of the azotometer is also filled with water. A graduated tube is now brought over the end, and by opening the tap and raising the reservoir the gas passes into the tube. The end is now closed with the thumb and transferred to a cylinder of water.

The tube is held by a collar of paper, whilst the level is adjusted and the volume and temperature noted.

Before commencing a second determination, the contents of the combustion tube are emptied on to the wire-gauze sieve, placed over one of the tin dishes, and the fine and coarse oxide separated. Both oxides are roasted in order to reoxidise any reduced copper, and transferred as before to their respective flasks. The sodium bicarbonate tube is emptied into a special bottle and then replenished with fresh material. Fresh caustic

potash solution is also introduced into the azotometer, unless the stronger solution is used.

Estimation of Nitrogen, Second Method.—Another method which dispenses with the small furnace and bicarbonate tube may also be used. The long combustion tube is closed at one end and magnesite in small lumps is introduced into the tube
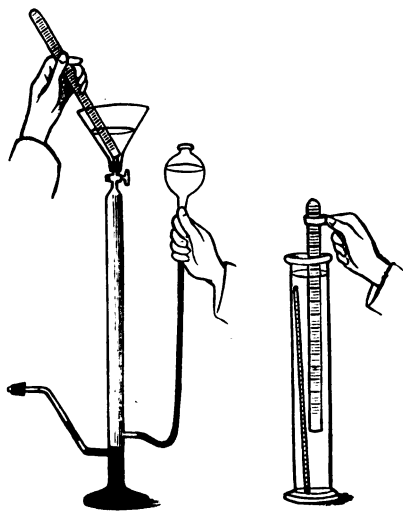
FIG. 16.

and shaken down to the closed end until there is a layer of about 13—15 cm. (5—6 in.) This is kept in place by a plug of asbestos and the tube is filled successively with 5 cm. (2 in.) of coarse copper oxide, then fine copper oxide mixed with the substance, a further layer of coarse copper oxide, and finally the copper spiral. The contents of the tube are arranged as shown in Fig. 17.

The magnesite ($MgCO_3$), which evolves carbon dioxide on heating, takes the place of the sodium bicarbonate in the previous method. The air is displaced at the beginning by heating the magnesite near the closed end of the tube. The

magnesite is again heated towards the end of the combustion to sweep out the last traces of nitrogen. The disadvantages of the method are that the magnesite requires to be heated much
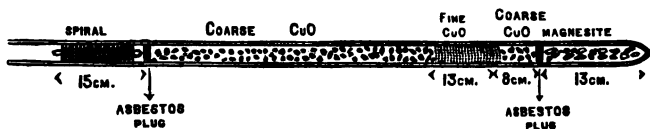
FIG. 17.

more strongly than the sodium bicarbonate before it evolves carbon dioxide, and the length of the layer of copper oxide is curtailed.

Estimation of the Halogens

Qualitative Examination.—Many halogen compounds impart a green fringe to the outer zone of the non-luminous flame. A more delicate test is to heat the substance with copper oxide. Heat a fragment of copper oxide, held in the loop of a platinum wire, in the outer mantle of the non-luminous flame until it ceases to colour the flame green. Let it cool down a little and then dust on some halogen compound (bromacetanilide will serve this purpose, see Prep. 50, p. 132.) Now heat again. A bright green flame, accompanied in the case of chlorine by a blue zone immediately round the oxide, indicates the presence of a halogen. The halogen in the majority of organic compounds is not directly precipitated by silver nitrate. Only those compounds which, like the hydracids and their metallic salts, dissociate in solution into free ions give this reaction. If, however, the organic compound is first destroyed, and the halogen converted into a soluble metallic salt, the test may be applied. Heat the substance with a fragment of metallic sodium or potassium as in the test for nitrogen, p. 11. The test-tube whilst hot is placed in cold water, the alkaline solution filtered, acidified with dilute nitric acid and silver nitrate solution added. A curdy, white or yellow precipitate (provided no cyanide is present), indicates a halogen.

Quantitative Estimation (Carius).—The method of

C 2

Carius, which is usually employed, consists in oxidising the substance with fuming nitric acid under pressure in presence of silver nitrate. The silver halide which is formed is then separated by filtration and weighed.

The following apparatus is required :—

1. *A piece of thick-walled soft tubing* about 35—38 cm. (14—15 in.) long, and 16—17 mm. inside diameter, the walls being at least 2·5—3 mm. thick. Tubes of hard potash glass are also used, in which case the thickness of the walls may be rather less. The tube is carefully sealed at one end so that there is no thickening of the glass at any point into a blob. If a blob is formed, it may be removed by heating it and blowing gently into the tube and repeating the operation if necessary.

FIG. 18.

Tubes of soft or hard glass may be bought ready sealed at one end. The tube is washed out and dried before use.

2. *A narrow weighing-tube*, 8—10 cm. (3—4 in.) long and sealed at one end, which will slip easily into the thick-walled tube.

3. *Pure fuming nitric acid of sp. gr.* 1·5.—This is prepared by distilling equal volumes of concentrated nitric acid (150 c.c.), and concentrated sulphuric acid (150 c.c.) from a litre retort, the neck of which has been bent in the blow-pipe flame as in Fig. 18. The object of this bend is to prevent acid from spirting into the neck and being carried over mechanically into the receiver during distillation. The retort is placed on a sand-bath, and attached to a condenser. The acids are poured in through a funnel, and a few small bits of broken unglazed pot are dropped in to prevent bumping. The acid is distilled with a

moderate flame until about 100 c.c. have collected in the receiver, when the operation is stopped. The distillate is then tested for halogens by diluting largely with distilled water, and adding silver nitrate solution. The liquid should remain perfectly clear. It should also be tested for the presence of sulphuric acid, in case it is required for sulphur estimations, by adding a few drops of barium chloride to a fresh portion of acid diluted as above. If pure, it is kept in a stoppered bottle. If it contains chlorine, it must be redistilled over a few crystals of
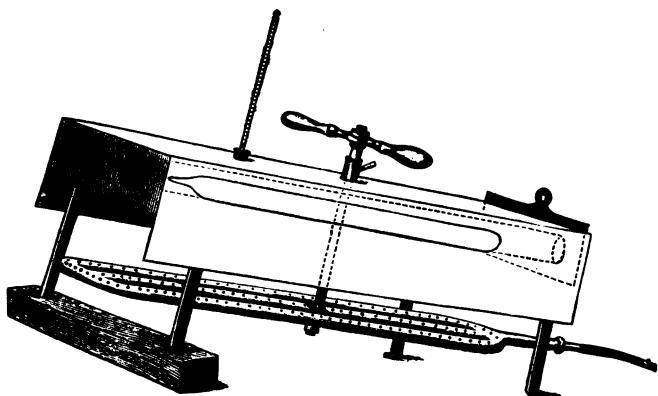
FIG. 19.

silver nitrate. Fuming nitric acid has a sp. gr. of about 1·5 at 15°, boils at about 90°, and contains about 90 per cent. of HNO_3.

4. *A Tube Furnace.*—Various forms of furnace are used. Those which are heated on the principle of the Lothar Meyer hot-air furnace by a number of pin-hole gas jets are easily regulated, and can be raised to a high temperature. The Gattermann furnace, shown in the diagram (Fig. 19) is a very convenient form.

Filling and Sealing the Tube.—By means of a thistle funnel with a long stem, about 5 c.c. of fuming nitric acid are first introduced, and the funnel carefully withdrawn so as not to wet the side of the tube. About ·5 gram silver nitrate in crystals is dropped in, and finally the narrow weighing-tube containing

·2—·3 gram of substance is slipped to the bottom of the tube
(see Fig. 20).   Bromacetanilide (see Prep. 50, p. 132) may be
used for this estimation.   The open end of the tube is now
sealed in the blow-pipe.   This operation requires some
care and a little skill.   About two inches of the tube at
the open end is very gradually heated by revolving
it for several minutes in the smoky flame of the
blow-pipe.   The tube is now grasped about the middle
with the left hand, and inclined at an angle of about
45°.   The blast is turned on slowly, and the end of
the tube heated and revolved until the glass begins to
soften.   The end of a glass rod, about 13 cm. (5 in.)
long, held in the right hand, is heated at the same
time.   The glass rod is then used to press the edges
of the glass tube together, as shown in Fig. 21.
The subsequent operation depends upon whether soft or
hard glass is to be manipulated.   If soft glass is used, the
blow-pipe flame is made as hot as possible, but reduced

FIG. 20.
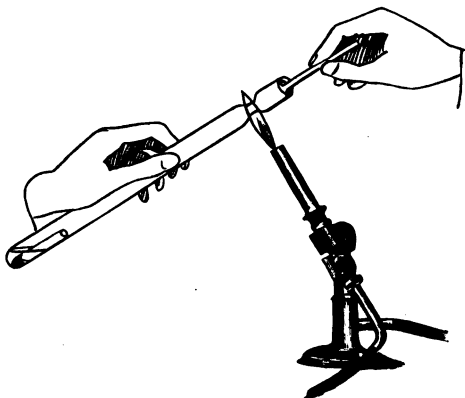
FIG. 21.

in length to about 8 to 10 cm. (3 to 4 in.).   It is directed at a
point about 2 to 3 cm. (1 in.) below the open end to which
the glass rod is attached, the glass rod now serving as a support
whilst the tube is slowly rotated.   The glass if evenly heated

and not drawn out, begins to thicken where the flame plays upon it, and the inside diameter of the tube contracts. When the apparent inside diameter of the tube is reduced to about 3 mm. ($\frac{1}{8}$ in.) (Fig. 22), the tube is quickly removed from the flame, and a capillary end formed by very slowly drawing out the thickened part of the tube (Fig. 23). When the capillary has so far cooled as to become rigid, it is sealed off. The tube will now have the appearance shown in Fig. 24. The tube is kept in a vertical position until cold. If the tube is of hard glass, a somewhat different method of sealing is employed. As soon as the glass is sufficiently soft, it is not thickened, but drawn out at once into
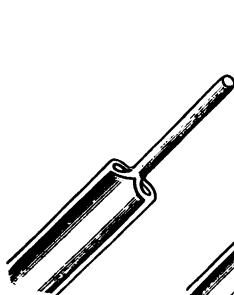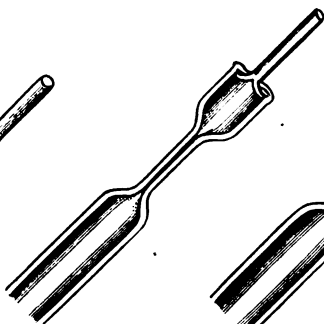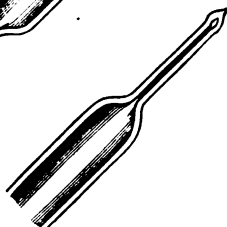
FIG. 22. FIG. 23. FIG. 24.

a wide capillary, about 1½ cm. long. By directing the flame below this constriction, and continuing to draw out, the capillary is further lengthened. When it has a length of 2 to 3 cm. (1 in.) it is thickened by revolving it in the flame and then sealed off. Hard glass is much more easily manipulated in the oxy-coal gas flame. When cold, the tube is transferred to the metal cylinder of the tube furnace. The furnace, conveniently isolated in case of explosions, should stand on the floor with the open end raised and facing a wall. The capillary point should project a little beyond the open end of the metal cylinder in which the sealed tube is enclosed. The temperature, indicated by a thermometer fixed in the top of the furnace, is carefully regulated. It is advisable to commence the operation in the morning. The temperature is gradually raised from 150° to 200°

during four hours, and then to 220° for a further four hours. The gas is then extinguished, and the tube allowed to cool until the following morning.

Opening the Sealed Tube.—The tube is drawn a little way out of the iron casing, so that the capillary end projects 3 or 4 cm. The tip is then warmed cautiously in the Bunsen flame to expel the liquid which as a rule condenses there. The point is then heated until the glass softens, when the pressure inside perforates the glass and nitrous fumes are evolved. *On no account must the tube be removed from the furnace before this operation is concluded.* The tube is now taken away and opened. A deep file scratch is made in the wide part of the tube, about 3 cm. below the capillary. The end of a glass rod, heated to redness, is then held against the file mark. A crack is produced, which may be prolonged round the tube by touching the tube in front of the crack with the hot end of the glass rod. The top of the tube is now easily removed ; but in order to prevent fragments of glass from the broken edge from dropping into the acid, the tube should be held nearly horizontally and the end carefully broken off. Any bits of glass which become detached adhere to the side of the tube, near the open end, and can be easily wiped off. The contents of the tube containing the silver halide are now carefully diluted by adding water a few c.c. at a time, and then washed into a beaker. The mixture is heated to boiling, the silver compound transferred to a filter, and washed with hot water until free from silver nitrate. The filter paper is then dried in a steam oven and the silver salt estimated in the usual way. The result is calculated in percentage of halogen.

Example—Bromacetanilide gave the following result :—

·151 gram gave ·134 gram AgBr.

$$\frac{·134 \times 80 \times 100}{188 \times ·151} = 37·51 \text{ per cent.}$$

Calculated for C_8H_8BrNO ; Br = 37·38 per cent.

Another Method (Piria and Schiff).—There are some substances which are incompletely decomposed with fuming nitric acid under the conditions described above, and the results are consequently too low. In such cases the following method

may be employed. The substance is weighed into a very small platinum crucible, which is then filled up with a mixture of anhydrous sodium carbonate (1 part) and pure powdered quicklime (4 to 5 parts). The crucible is then inverted in a larger crucible, the space between the two being filled with the same mixture of sodium carbonate and lime. The large crucible is now heated, first with a small blow-pipe flame, and then more strongly until the mass is red hot. The contents are then allowed to cool, and dissolved in a large excess of dilute nitric acid. The substance must be added slowly and the acid kept cool. The halogen is then precipitated with silver nitrate and estimated in the usual way.

Estimation of Sulphur

Qualitative Examination.—The presence of sulphur in organic compounds may be detected by heating the substance with a little metallic sodium or potassium. The alkaline sulphide, when dissolved in water, gives a violet colouration with a solution of sodium nitroprusside. Heat a fragment of gelatine with a small piece of potassium in a test-tube until the bottom of the tube is red hot, and place it in a small beaker of water as described in the test for nitrogen (p. 11). Filter the liquid and add a few drops of sodium nitroprusside solution.

Quantitative Estimation (Carius).—The process is essentially the same as that described under the estimation of halogens (p. 20). The compound is oxidised in a sealed tube with fuming nitric acid, but without the addition of silver nitrate. The resulting sulphuric acid is then precipitated and weighed as barium sulphate. The same quantities of acid and substance (diphenylthiourea may be used, see Prep. 55, p. 138) are taken, and the process of sealing up and heating, &c., are carried out in precisely the same way as for the halogens. The contents of the tube, after heating, are cautiously diluted with water and then washed out into a beaker, and filtered, if necessary, from fragments of glass. The filter paper is then well washed with hot water and the filtrate diluted to at least 250 c.c. with water. The liquid is heated to boiling, and a few c.c. of barium chloride solution added. On continued heating over a small flame the liquid clears and the precipitate subsides. The

addition of another drop of barium chloride will determine if the precipitation is complete. The liquid is then filtered, the precipitate of barium sulphate washed with hot water, dried and weighed in the usual way.

Example—Diphenylthiourea gave the following result :—

·2518 gram gave ·2638 gram $BaSO_4$

$$\frac{·2638 \times 32 \times 100}{233 \times ·2518} = 14·39 \text{ per cent.}$$

Calculated for $C_{13}H_{12}N_2S$; S = 14·05.

Determination of Molecular Weight

According to Avogadro's law, equal volumes of all gases under similar conditions contain the same number of molecules. Consequently the weights of equal volumes or the densities of gases will represent the ratio of their molecular weights. If the densities are compared with hydrogen as the unit, the ratio

$$\Delta = \frac{W_s}{W_h}$$

in which W_s and W_h are the weights of equal volumes of substance and hydrogen respectively, will give the molecular weight of the substance compared with the molecule or two atoms of hydrogen or half the molecular weight compared with one atom of hydrogen. Consequently the observed density must be multiplied by two in order to obtain the molecular weight compared with one atom of hydrogen.

Vapour Density Method (Victor Meyer).—This method, which is generally employed for substances which volatilise without decomposition, is known as the *air displacement* method of Victor Meyer. It consists in rapidly vaporising a known weight of the substance at a constant temperature at least 40°—50° above its boiling point in a special form of apparatus, which admits of the displaced air being collected and measured. The volume occupied by a given weight of the substance under known conditions is thus ascertained and from these data the density is calculated. The following apparatus is required :—

1. *A Victor Meyer Apparatus* as shown in Fig. 25. It consists of an elongated glass bulb with a narrow stem and a capillary side tube. It is provided with a well-fitting rubber cork; which can be pressed easily and tightly into the open end of the stem. The apparatus is clamped within an outer jacket of tin plate or copper, which holds the boiling liquid required to produce a constant temperature. It is represented as transparent in the Figure.
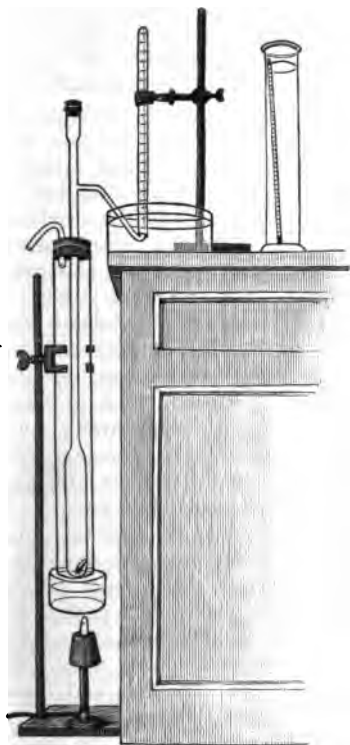
FIG. 25.

2. *Hofmann Bottles.*— The substance, if liquid, is introduced into a small stoppered glass bottle known as a Hofmann bottle (see Fig 26). The dry bottle with the stopper is carefully weighed and then filled with liquid through a tube drawn out into a wide capillary. The stopper is inserted and the bottle reweighed. It should hold about ·1 gram of substance.

3. *A narrow graduated tube* holding 50 c.c. and divided into tenths of a c.c.

4. *A large crystallising dish*

FIG. 26.

which serves as a gas trough.

5. *A long and wide cylinder* in which the graduated tube can be submerged in water.

6. *A Bunsen burner with chimney*.

The apparatus is set up as shown in Fig. 25. The Victor

Meyer apparatus is thoroughly dried by blowing air through by means of a long glass tube, which reaches to the bottom of the bulb. A small quantity of clean dry sand previously heated in a crucible or a pad of asbestos is placed at the bottom of the bulb to break the fall of the Hofmann bottle, when it is dropped in. The bulb of the outer jacket is filled two-thirds full of water and the displacement apparatus is clamped within it, so that it nearly touches the liquid. The apparatus and jacket must be adjusted at such a height that the capillary side limb dips under the water contained in the crystallising dish, placed on the bench. The graduated tube is filled with water and inverted under the water in the crystallising dish and clamped there until required. The burner protected from draughts by the chimney is lighted under the outer jacket and the displacement apparatus left open at the top. To avoid inconvenience arising from the steam, a split cork, into which a bent glass tube is inserted, is pushed loosely into the open end of the jacket.

Whilst the water is boiling steadily and not too violently, the substance is weighed. Chloroform, b.p. 61°, or pure and dry ether, b.p. 34·5° (see Prep. 3, p. 52), may be used for the experiment, as their boiling points lie well below that of water. Before introducing the bottle and liquid, the apparatus must be tested to ascertain if the temperature is constant. As a rule ¼ hour's boiling suffices. Push in the rubber cork and note if within the next minute or two any bubbles escape. If not, slip the graduated tube over the end of the side tube, and carefully remove the rubber cork so that no water enters the stem through the capillary. Remove the stopper of the Hofmann bottle before dropping it in, and at once push in the cork. Very shortly a stream of air bubbles will ascend the graduated tube. When, in the course of a minute or two, the bubbles cease, remove the cork from the apparatus and extinguish the burner. The graduated tube is transferred to the large cylinder of water by closing the open end with the thumb. Leave the tube in the water with a thermometer beside it for ¼ hour. Lift the graduated tube, and whilst holding it by a collar of paper adjust the levels inside and out. Read off the volume and note the temperature and barometric pressure.

The density is calculated as follows :—

If v is the volume, t the temperature, B the barometric

pressure, and f the vapour tension of water at $t°$, then the corrected volume is given by the formula

$$\frac{v \times (B - f) \times 273}{760 \times (273 + t)}$$

This multiplied by ·00009, the weight of 1 c.c. of hydrogen, gives the weight of hydrogen occupying the same volume as the vaporised substance, from which the density $\Delta = \dfrac{W_s}{W_h}$ is obtained.

Example—The following result was obtained with ether : ·1146 gram of ether gave 36·3 c.c. at 11° and 752 mm. $f = 10$ mm. at 11°.

$$\frac{36·3 \times (752 - 10) \times 273 \times ·00009}{760 \times 284} = ·00306.$$

$$\frac{·1146}{·00306} = 37·4$$

Calculated for $C_4H_{10}O$; $\Delta = 37$.

If substances of higher boiling point have to be vaporised, the water in the outer jacket is replaced by other liquids of correspondingly higher boiling point, such as xylene, b.p. 140°, aniline, b.p. 182°, ethyl benzoate, b.p. 211°, amyl benzoate, b.p. 260°, diphenylamine, b.p. 310°, &c. A Lothar Meyer air-bath (Fig. 27) is, however, much more convenient for obtaining constant temperatures up to 600°. It consists of three concentric metal cylinders, the outer one being coated with non-conducting material. They are so arranged that the heated air from a movable ring burner passes between the two outer

FIG. 27.

cylinders (shown in section in the Fig.), and descends to the bottom of the central cylinder, into which it has access through
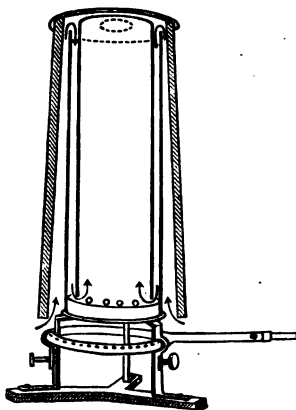
a ring of circular holes. The hot air is thoroughly mixed by this zig-zag flow, and the temperature is equalised. The bulb of the displacement apparatus is clamped in the interior cylinder, and a thermometer is fixed beside it.

The vapour density of freshly distilled aniline, b.p. 182°, may be determined, the temperature of the air-bath being adjusted to about 240°. The adjustment is made by raising or lowering the flame, or by altering the position of the movable ring burner.

Example—·1229 of aniline gave 31 c.c. at 7·5° and 750 mm.

$$\Delta = 45·87.$$

Calculated for C_6H_7N ; $\Delta = 46·5$

The Cryoscopic or Freezing-point Method (Raoult).

—This method depends upon the fact, first demonstrated by Raoult, and afterwards confirmed on theoretical grounds by van't Hoff, that the original freezing-point of a given quantity of liquid is lowered the same number of degrees by dissolving in it different substances whose weights are proportional to their molecular weights. This rule does not however apply to salts, acids, &c., which appear to dissociate in certain solvents, nor to substances which form molecular aggregates or *associate* in solution. Supposing the freezing-point of 100 grams of a solvent to be lowered 1° by dissolving 1, 2, 3 and 4 grams respectively, of four different substances, the molecular weights of these substances will be in the ratio of 1 : 2 : 3 : 4. In order to convert these ratios into true molecular weights, the numbers must be multiplied by a coefficient which depends upon the nature of the particular solvent selected, and which may be determined empirically by means of substances of known molecular weight or by calculation from thermodynamical data.[1]

If w is the weight of substance and W the weight of solvent, d the depression of the freezing-point, and C the coefficient for the solvent determined for the standard conditions, *i.e.*, for the weight of substance, which produces 1° depression in 100 grams

[1] *Vide* van't Hoff, *Ztschr. Phys. Chem.*, i. p. 481 ; Ostwald, *Outlines of General Chemistry*, chap. vi. p. 139 ; J. Walker, *Introduction to Physical Chemistry*, chap. xviii. p 176.

of solvent, the molecular weight M is given by the following expression :—

$$M = \frac{100\ Cw}{dW}.$$

The values of C for the common solvents in use are as follows :—

Water ...	...	18·8.
Benzene	...	50.
Phenol...		75.
Acetic Acid	...	39.

The following apparatus is required :—

A Beckmann Freezing-point Apparatus.—The form of apparatus is shown in the accompanying Fig. 28. It consists of a glass jar standing on a metal tray and furnished with a stirrer. The cover of the jar has a wide slit to admit the stirrer, and a circular aperture with clips to hold a wide test-tube.

Within the wide test-tube is a narrower one, which is held in position by a cork. The narrow test-tube is sometimes furnished with a side tube, for introducing the substance, but it is not necessary. It is provided with a stirrer. A Beckmann thermometer completes the apparatus. This is fixed through a cork so that the bulb nearly touches the bottom of the tube, a wide slit being cut in the side of the cork for moving the stirrer. The Beckmann thermometer is of special construction and requires explanation. As the method involves merely an accurate determination of small differences of temperature, it is not requisite to know the exact position on the thermometer scale. The Beckmann thermometer registers 6 degrees, which are divided into hundredths. The little glass reservoir at the top (*a*, Fig. 28) serves the purpose of adjusting the mercury column to different parts of the thermometer scale by adding or removing mercury from the bulb.

Freezing-point Determination.—In the example to be described, pure benzene (see p. 120) is used as the solvent. Carefully dry the inner tube. Fit it with a cork and weigh it together with the cork suspended by a wire to the arm of the balance. Introduce sufficient benzene to cover the bulb of the Beckmann thermometer when it is pushed nearly to the bottom of the

tube. About 10 c.c. will be found to be sufficient. Insert the cork and weigh the tube and benzene. Fill up the outer jar with water and small lumps of ice and stir from time to time.
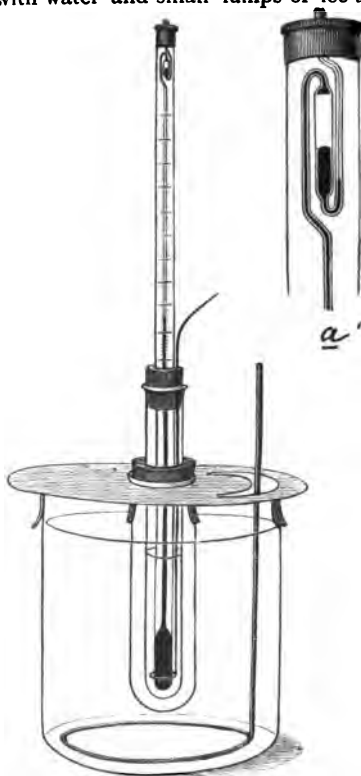
Whilst the benzene is cooling in the apparatus the Beckmann thermometer may be adjusted.

Adjustment of the Beckmann Thermometer.—Determine first the value of the mercury thread in degrees between the top of the scale and the orifice of the reservoir. This may be done by warming the bulb in a water-bath along with an ordinary thermometer. As soon as sufficient mercury has collected at the orifice, the burner is removed, the water well stirred, and the little bead of mercury detached by gently tapping the head of the thermometer without removing the bulb from the water. The temperature on the ordinary thermometer is noted and is again read off when the mercury in the Beckmann thermometer has subsided to the top of the scale.

Fig. 28.

Supposing, then, the value of the thread above the scale to have been determined and equivalent to $2°$, and the freezing-point of benzene to be about $4°$, the thermometer degrees may in this case be made to coincide with the Beckmann degrees, which will bring the thread of mercury well up the scale. The bulb of the thermometer will therefore require to be at a temperature of $6 + 2 = 8°$

before removing the excess of mercury. It will, however, be necessary to introduce more mercury into the bulb. This is done by inverting the thermometer and tapping it gently on the palm of the hand, so as to detach a bead of mercury, which slips down to the orifice of the capillary. By warming the bulb the mercury is driven to the top and coalesces with that in the reservoir, so that on cooling the additional mercury runs into the bulb. When sufficient mercury has been added the thermometer is cooled to 8°, and the excess detached as described above. The zero should now coincide approximately with that of ice-cold water. If the thermometer is to be adjusted to any other temperature it is placed in water and warmed to that temperature + the number of degrees on the scale above that point + the value of the thread above the scale. The excess of mercury is then detached. The thermometer being adjusted, insert it through the cork so that the bulb is well covered by the benzene, and let the benzene cool well below its freezing-point before stirring. Tap the head of the thermometer occasionally with a pencil. Now stir briskly for a moment. As soon as crystals of the solvent begin to separate the mercury thread will shoot up. Keep stirring occasionally and tapping the thermometer, and read off the maximum point reached by means of a lens. This gives a rough indication of the freezing-point of the benzene. Take out the inner tube and melt the crystals by warming the tube in the hand, and replace it in the apparatus. Repeat the experiment, cooling the solvent not more than ·2° below its freezing-point before stirring. Make two or three determinations in this way. The results should not differ by more than ·01°. Fuse some naphthalene in a basin and break it up into small lumps. Weigh a piece of about ·1 to ·2 gram on a watch-glass. Raise the cork of the inner tube and drop the naphthalene in. Let it dissolve and then determine the freezing-point of the benzene as before. Repeat the process by dropping one or two fresh pieces of naphthalene into the same solvent. At the end of the operation remove the thermometer and stirrer, and weigh the benzene in the inner tube with the cork. After deducting the weight of naphthalene, the weight of the benzene will be approximately the mean of the first and final weighings.

Example.—Using the same solvent and adding successively

three lots of substance (naphthalene), the following results were obtained :—

	w.	W.	a.	M.	Mean.
1	·0985	9·7	·403	126	
2	·0729	,,	·305	123·2	125·3
3	·1193	,,	·486	126·8	

Calculated for $C_{10}H_8$; $M = 128$.

The Eykman Depressimeter.—For rapid but less accurate determinations the apparatus of Eykman may be used, which is shown in Fig. 29. It consists of a small vessel, into the neck of which a thermometer is ground. The thermometer

is of the Beckmann type but divided into twentieths of degrees. Phenol, m.p. 42°, is usually employed as the solvent. The vessel and thermometer are dried and weighed. Phenol melted on the water-bath is poured in to within about 5 c.c. of the neck, the thermometer inserted, and the apparatus weighed again. The melting-point of the phenol must now be ascertained. Warm the vessel over a small flame on a sand-bath so as to melt the phenol, leaving, however, a few crystals floating in the liquid, and place the vessel in the cylinder, at the bottom of which is a wire spring or pad of cotton wool. A perforated cork at the top keeps the stem of the thermometer in position. Let the phenol cool down well below its freezing-point, and then shake the cylinder until solidification commences. This will give a first approximation to the freezing-point. The phenol is now warmed gently as before until only a few crystals remain unmelted. The vessel is replaced in the cylinder and the liquid cooled ·5 to 1° below the point previously ascertained. It is now shaken until crystallisation sets in, and then occasionally until the maximum point is reached. The operation is repeated as often as requisite. The substance is now introduced, a sufficient quantity being taken to produce a depression of at least ·5°. In order to effect this, the phenol is melted and the neck warmed with a small flame until the thermometer is loosened and can be withdrawn. As much phenol as possible is allowed to drain off the neck

FIG. 29.

and off the thermometer, and the weighed quantity of substance introduced. The thermometer is replaced, and any phenol which may have run out is wiped off from the outside of the vessel, which is then re-weighed. The freezing-point is determined as before.

The Boiling-point Method (Raoult).—The boiling-point of a liquid is found to be affected by the presence of a dissolved substance in a similar manner to the freezing-point, that is, the boiling-point of a given quantity of a liquid is *raised* the same number of degrees by dissolving in it the same number of molecules of different substances, or, in other words, such weights of these substances as represent the ratio of their molecular weights. These facts were first clearly demonstrated by Raoult. The most convenient form of apparatus for determining molecular weights by this method is Beckmann's boiling-point apparatus shown in Fig. 30.

It consists of a boiling tube, through the bottom of which a stout platinum wire is sealed, which is intended to conduct external heat to the liquid and form bubbles at one point. Above the wire is a layer, about an inch deep, of glass beads. The object of the beads is to break up the bubbles and so prevent superheating and irregular boiling. To the side limb a reflux condenser is attached to condense the vapours given off during the boiling. A Beckmann thermometer is inserted through the mouth of the tube. This thermometer is similar in construction to that used for freezing-point determinations, but it has a smaller bulb. The boiling tube is placed in the central cavity of a hollow glass or porcelain jacket, which contains the same liquid as the boiling tube and is also provided with a condenser. This jacket prevents radiation from the boiling tube. It is provided with two windows of mica. The jacket is clamped on a gauze ring supported on a square tray of asbestos placed upon a tripod. In the figure the lower part of the porcelain jacket and the asbestos tray are made transparent to show the position of the burners and the concentric rings of asbestos below the tray. The asbestos has a circular hole in the centre, which admits the lower end of the boiling tube. Two asbestos chimneys are fixed upright at the diagonal corners of the tray to carry off heated air, and two burners are placed below the other two corners. The boiling-point of the solvent is first ascertained.

For this purpose benzene may be used. The Beckmann thermometer must be adjusted so that, when in the boiling liquid, the thread occupies the lower half of the scale. In order to adjust it, the bulb must be placed in water warmed gradually 6°—7° above the boiling-point of benzene, and the bead then detached as already explained in the description of the freezing-point method.
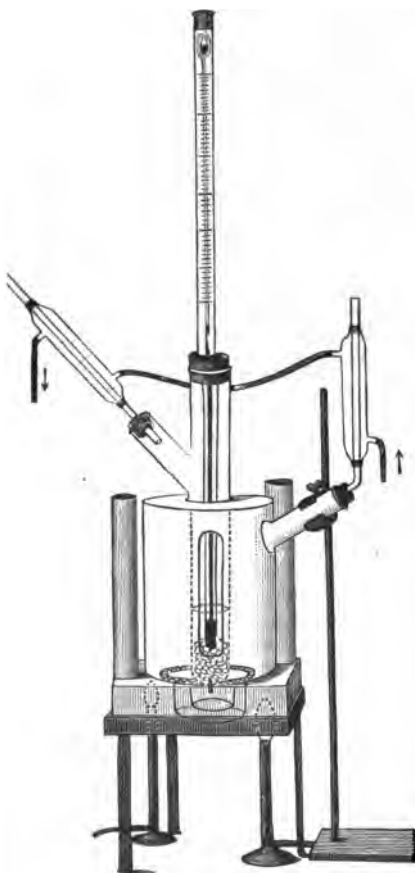
The boiling tube is carefully dried and weighed with the beads. Sufficient benzene is poured in to cover the bulb of the thermometer, which is pushed down a little way into the beads. The condenser is attached to the side limb. A layer of 1—2 cm. of benzene is poured into the outer jacket, and the condenser fixed in position. The same water supply may be made to traverse both condensers. The two burners under the tray are lighted and the temperature regulated so that the benzene in the outer jacket boils briskly, whilst at the same time sufficient heat finds its way to the boiling tube,

FIG. 30.

through the gauze ring outside the concentric screens of asbestos below the tray, to keep the benzene in the state of steady ebullition. In about ¼ hour from the time the benzene boils in the inner tube the first reading may be made, and a fresh reading every five minutes until the temperature is constant, *i.e.* does not vary more than ·01°. As the atmospheric pressure may produce considerable variations in the reading, it is important to observe the barometer occasionally during the experiment, and to make a correction, which is about ·043° for every ·1 mm. below 760.

The temperature being constant, a pellet (·1—·2 gram) of fused naphthalene is carefully weighed and dropped into the boiling-tube through the condenser without interrupting the boiling. These pellets are conveniently made in a small bullet-mould.

The boiling-point will rise and after a few minutes will remain stationary. The temperature is noted. A second and third determination may be made by introducing fresh pellets of naphthalene.

When the observations are complete, the apparatus is allowed to cool and the weight of benzene ascertained by weighing the boiling-tube and benzene.

As in the freezing-point method, the molecular weight is calculated from the weight of substance required to raise the boiling-point of 100 grams of solvent 1°, and the result multiplied by a coefficient which depends upon the nature of the solvent. The following is a list of solvents commonly employed and their coefficients :—

Water ...	...	5·2
Alcohol	...	11·5
Ether ...	...	21·1
Acetic Acid	...	25·3
Benzene	...	26·7
Aniline	...	32·2
Chloroform	...	36·6

The molecular weight is determined from the formula

$$M = \frac{100\,Cw}{d\,W},$$

in which w is the weight of substance, W that of the solvent, d the rise of boiling-point, and C the coefficient.

Example—Using the same solvent and adding successively four pellets of naphthalene, the following results were obtained :—

	w.	W.	d.	M.	Mean.
1	·1866	21·313	·185	126·6	
2	·1893	,,	·185	128·3	128·3
3	·1860	,,	·185	126·0	
4	·1901	.,	·180	132·4	

Calculated for $C_{10}H_8$; M = 128.

Although the method is able to dispose of a greater number of convenient solvents than are adapted for freezing-point determinations, it is never so accurate, mainly on account of the difficulty of avoiding fluctuations in the boiling-point, due to radiation, to the dripping of cold liquid from the condenser, and to barometric fluctuations.

Molecular Weight of Organic Acids

Determination by means of the Silver Salt.—The basicity of an organic acid being known, the molecular weight can be determined by estimating the amount of metal in one of its normal salts. The ratio of metal to salt will be that of the atomic weight of the metal to the molecular weight of the salt. The silver salts are usually selected for these determinations, since they are, as a rule, normal, *i.e.* neither acid nor basic ; they are only slightly soluble in water, and are consequently readily obtained by precipitation, and finally they contain, as a rule, no water of crystallisation. On the other hand they are very unstable, being quickly discoloured when exposed to light, and often decomposing with slight explosion when heated. Silver benzoate may be prepared by way of illustration. Weigh out roughly 2—3 grams of benzoic acid into a flask, and add about 20 c.c. of water and an excess of dilute ammonia. Boil the solution until the escaping steam has nearly lost the smell of ammonia, and then test the liquid from time to time until it is neutral to litmus. Cool the flask under the tap, and add an excess of silver nitrate solution (3—4 grams, $AgNO_3$). Filter with the filter-pump. A filter-pump is an essential part of a laboratory fit-

ting. It consists of a good water-jet aspirator (see Fig. 31), which is fixed to the water-tap by a stout piece of rubber tubing well wired at both ends. The joint is wrapped round with cloth or leather wired on to the rubber. The side tube of the aspirator is connected by *pump tubing* to an empty filter flask or bottle by means of a glass tap. A second glass tube or side piece is put in connection with the filter flask by means of rubber tubing. The object of inserting a vessel between the pump and the filter flask is to prevent water running back when the aspirator is stopped. Before stopping the pump, close the glass tap. Turn off the water, and then lift the tap out of its socket for a moment to equalise the pressure.

Use a porcelain funnel and filter flask, different sizes of which are shown in Fig. 32. The bottom of the funnel is covered with

FIG. 31.

a disc of filter paper. After filtering, wash three or four times with a little cold water, press the precipitate well down and let it drain. Remove the precipitate and spread it on a piece of porous plate, and place it in a vacuum-desiccator over sulphuric acid. There are several useful forms of vacuum-desiccator, two of which are represented in Fig. 33.

The ground rims are greased with vaseline or a mixture of bees-wax and vaseline, and the air is exhausted by attaching the tube of the water-pump to the glass tap of the desiccator.

If the substance is left over night in the desiccator it will be dry by the next day. The silver salt should be protected as far
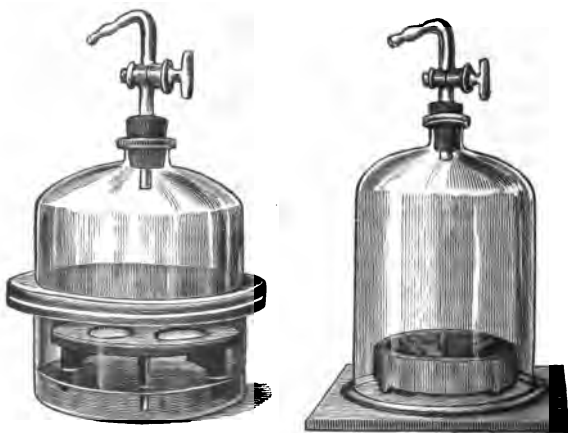
FIG. 32.

FIG. 33.

as possible from the light. When the precipitate is thoroughly dry, weigh about ·3 gram into a weighed porcelain crucible. Cover with the lid and heat, at first gently, over a small flame. When the first reaction is over, heat the crucible for a few minutes to a dull red heat, and then allow it to cool in a desiccator. The silver salt will be completely decomposed and leave a dull white residue of silver. The crucible is now weighed and the weight of silver determined.

If W is the weight of salt, w the weight of silver, and n the basicity of the acid, the molecular weight of the silver salt is determined from the following formula :—

$$\frac{W \times 108\, n}{w}$$

The molecular weight of the acid is then obtained by deducting n atoms of silver and adding n atoms of hydrogen.

Example—·3652 grm. silver benzoate gave ·1720 grm. silver.

$$\frac{108 \times ·3652}{·1720} - 108 + 1 = 122·2$$

Calculated for $C_7H_6O_2$; $M = 122$.

Molecular Weight of Organic Bases

Determination by Means of the Platinum Salt.—
The organic bases form, like ammonia, crystalline chloroplatinates with platinic chloride of the general formula $B_2H_2,PtCl_6$. By estimating the amount of platinum present in the salt, it is possible to calculate the molecular weight of the platinum compound, and consequently that of the base.

Dissolve about 1 gram of freshly distilled aniline in a mixture of equal volumes of concentrated hydrochloric acid and water until a drop of the solution turns a piece of filter paper coloured with methyl violet a green colour (about 4 c.c.). To the clear hot solution add excess of platinic chloride and let it cool. Yellow crystalline plates of the chloroplatinate $(C_6H_5NH_2)_2H_2PtCl_6$ separate out.

Filter on the porcelain funnel with the pump and wash three or four times with small quantities of a cold mixture of equal volumes

of water and strong hydrochloric acid. Press the precipitate down and dry on a porous plate over solid caustic potash in the vacuum-desiccator.   When thoroughly dry, weigh out about ·5 to 1 gram of the compound into a porcelain or platinum crucible, and heat gently with the lid on, and then more strongly until the organic matter is completely burnt away. Cool the crucible in the desiccator and weigh.

The molecular weight of the salt is calculated from the weight, w of the platinum, and W of the salt, according to the formula (the atomic weight of platinum being 195)

$$\frac{W \times 195}{w}$$

To determine from this the weight of the base, it is necessary to deduct from the molecular weight of the salt that of H_2PtCl_6, and as 2 molecules of the base are contained in the salt, the result is halved.

Example—·7010 grm. of the salt $(C_6H_5NH_2)_2H_2PtCl_6$ gave ·2303 grm. platinum.

$$\frac{·7010 \times 195}{·2303} = 594·2. \text{ M. W. of the salt.}$$

$$\frac{594·2 - 409·9}{2} = 92·15$$

Calculated for $C_6H_5NH_2$; M = 93.

Preparations

General Remarks.—Carefully read through the method. References to the process are given under each heading. Be clear as to the objects of the various steps described and the nature of the materials employed. It cannot be too strongly urged that in all cases where any doubt exists as to the nature or an operation, a preliminary trial should be made in a test-tube with a small quantity of the substance.   This is especially necessary in crystallisation where the quantity and character of the solvent is unknown.   A vast amount of time and material is thereby saved.   A small stock of clean and dry test-tubes (5 × ⅝ and smaller sizes) should always be at hand for this purpose ; also watch-glasses for microscopic examination of solid substances.

The yield of either the crude or purified product should

always be ascertained, and the purity of the product determined either by the boiling-point or melting-point. A small rough balance with celluloid pans, for use on the bench, is indispensable.

Select vessels of a size appropriate to the quantities dealt with. Never use beakers for boiling or evaporating liquids, but flasks and basins. The *reactions* described at the end of each preparation are to be done in test-tubes, and should not be neglected.

Above all, work with suitable, compact, and clean apparatus on a *clean bench*. The best results are usually obtained when the preparation is carried out with something of the care and accuracy of a quantitative analysis.

Where the *asterisk* occurs, it signifies that the operation must be conducted in the fume-cupboard.

Whilst the preparation is in progress, utilise the spare minutes in reading the notes in the *Appendix*.

Purification of Methylated Spirit

Methylated spirit may generally replace the more costly absolute alcohol as a solvent after undergoing a process of purification. The spirit must be of the old kind, consisting of a mixture of 9 parts spirit of wine and 1 part purified wood-spirit, without the addition of paraffin, *i.e.*, it should give a clear solution with water.

It contains, in addition to ethyl and methyl alcohols, water, fusel-oil,

FIG. 34.

acetaldehyde, and acetone. It may be freed from aldehyde by boiling with 2—3 per cent. solid caustic potash on the water-bath with an upright condenser for an hour, or if larger quantities are employed, a tin bottle is preferable, which is heated directly over a small flame (see Fig. 34). It is then

distilled with the apparatus shown in Fig. 35. The **bottle**
is here surmounted with a **T**-piece holding a thermometer.
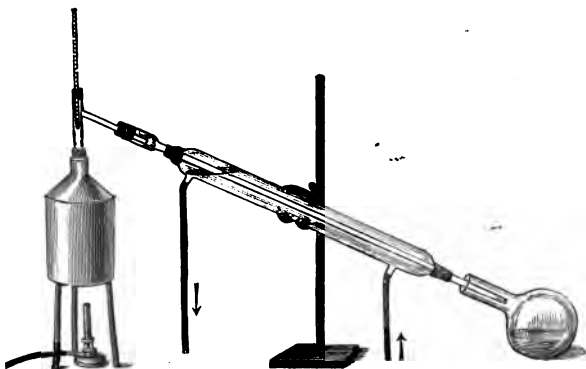The distillation is stopped when most of the spirit has distilled

FIG. 35.

and the thermometer reaches 80°. A further purification may
be effected by adding a little powdered permanganate of potash
and by a second distillation, but this is rarely necessary.

Ethyl Alcohol, $C_2H_5.OH$

Commercial absolute alcohol may be used for the preparations
which follow. It is obtained by distilling crude spirits of wine
over quicklime, and usually contains about ·5 per cent. of
water.

Properties.—Pure ethyl alcohol boils at 78·3°, and has a
sp. gr. of ·793 at 15°. It mixes with water in all proportions.

Reaction.—A delicate test for ethyl alcohol is the *iodoform
reaction.* Pour a few drops of alcohol into a test-tube and add
about 5 c.c. of a solution of iodine in potassium iodide, and then
dilute caustic soda solution until the iodine colour vanishes.
Shake up and warm very gently to about 60°. If no turbidity
or precipitate appears at once, set the test-tube aside for a
time. Yellow crystals of iodoform will ultimately deposit, which

have a peculiar odour, and a characteristic star shape when viewed under the microscope. The same reaction is given with other substances, such as acetone, aldehyde, &c., but not with methyl alcohol.

PREPARATION I.

Potassium Ethyl Sulphate, $C_2H_5O.SO_2.OK$

Dabit (1800), *Ann. Chim. Phys.* (1) 34, 300 ; Claesson (1879), *J. Prakt. Ch.* (2) 19, 246.

> 70 grms. (87 c.c.) absolute alcohol.[1]
> 50 ,, (27 c.c.) conc. sulphuric acid.

The alcohol is poured into a round flask ($\frac{1}{2}$ litre) and the sulphuric acid is slowly added and well mixed by shaking. A

FIG. 36.

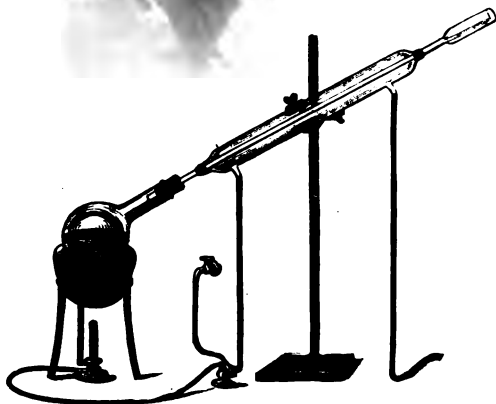considerable amount of heat is developed in the process. The flask is now fitted with an upright condenser (see Fig. 36) placed upon the water-bath and heated for 2—3 hours. The product now contains in addition to ethyl hydrogen sulphate, free

[1] For the preparation of methyl potassium sulphate the same quantity of methyl alcohol is used ; in other respects the two processes are identical. The yield is 45—50 grams.

sulphuric acid and unchanged alcohol. The liquid on cooling is poured into ½ litre of cold water in a large basin and well stirred. It is neutralised by adding chalk ground into a thin paste with water. This precipitates the free sulphuric acid as calcium sulphate and converts the ethyl hydrogen sulphate into the soluble calcium salt. The mixture is filtered through a large porcelain funnel (see Fig. 32, p. 40) at the filter-pump, and the precipitate pressed well down. The clear filtrate is heated on the water-bath and a solution of potassium carbonate (about 50 grams) is added in small quantities until the liquid is slightly alkaline. The calcium salt is thereby converted into the soluble potassium salt and calcium carbonate is precipitated. The latter is removed by filtration, as before, and the filtrate concentrated on the water-bath until a drop of the liquid, removed on the end of a glass rod, crystallises at once on cooling. The potassium ethyl sulphate is filtered, washed with a little methylated spirit,[1] and dried on a thin pad consisting of three or four sheets of filter paper, with another sheet over the crystals to keep out the dust. On concentrating the mother liquors on the water-bath, a further quantity of crystals may be obtained. Yield 35–40 grams. The substance should now be recrystallised from methylated spirit. With this object it is placed in a round flask attached to an upright condenser and heated on the water-bath. The form of apparatus is that already described (see Fig 36). Small quantities of methylated spirit are added and kept boiling until a solution is obtained. A small quantity of impurity may remain undissolved. The hot solution is at once decanted or filtered through a fluted filter (Fig. 37) into a beaker and allowed to cool. The following equations express the chemical reactions which occur :

1. $C_2H_5OH + H_2SO_4 = C_2H_5SO_4H + H_2O$
            Ethyl hydrogen sulphate.

2. $2C_2H_5SO_4H + CaCO_3 = (C_2H_5SO_4)_2Ca + H_2O + CO_2$
                        Calcium ethyl sulphate.

3. $(C_2H_5SO_4)_2Ca + K_2CO_3 = 2C_2H_5SO_4K + CaCO_3.$
                        Potassium ethyl sulphate.

---

[1] The methylated spirit which is used in this and all subsequent preparations must be purified according to the method described on p. 43.

Properties. Colourless, foliated crystals; easily soluble in water and dilute alcohol, less soluble in absolute alcohol.

Reactions. 1. Dissolve a little of the recrystallised salt in water and add barium chloride solution. There is no precipitate, as the barium salt of ethyl hydrogen sulphate is soluble in water. 2. Boil a little of the solution of the salt with a few drops of dilute hydrochloric acid for a minute and add barium chloride. A precipitate of barium sulphate is formed, as, on boiling ethyl
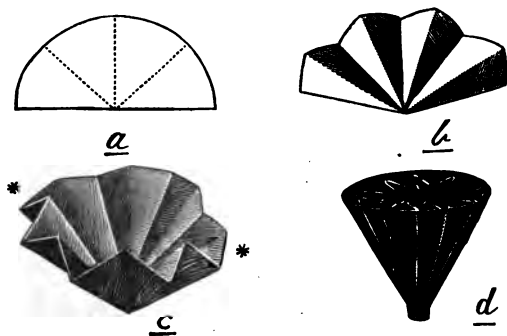
FIG. 37.

hydrogen sulphate in aqueous solution, it is decomposed into sulphuric acid and alcohol.

A fluted filter is made by first folding a large circular filter paper in the ordinary way. It is then half opened out and the two quadrants folded towards the middle line (see *a* Fig. 37). This makes three creases with the hollows on the same side. The filter is now turned over and each section folded down the centre so that the hollows of the four new creases alternate with the ridges of the three others as shown at *b*. The paper when opened now appears like *c*. The two rectangular flutings indicated by an asterisk have still to be divided by a crease down the middle. The filter is now pushed well into the funnel, the stem of which is cut off short as shown at *d*.

Ethyl Bromide (Monobromethane), C_2H_5Br.

De Vrij, *Jahresber.*, 1857, 441.

> 100 grms. potassium bromide.
> 100   „   (54 c.c.) conc. sulphuric acid.
> 60   „   (75 c.c.) absolute alcohol.

Fit up the apparatus as shown in Fig. 38. The distilling flask should have a capacity of not less than 1 litre, and is attached to a long condenser. An adapter is fixed to the end of the condenser, dipping into a conical flask (250 c.c.), which serves as receiver. The alcohol and sulphuric acid are mixed
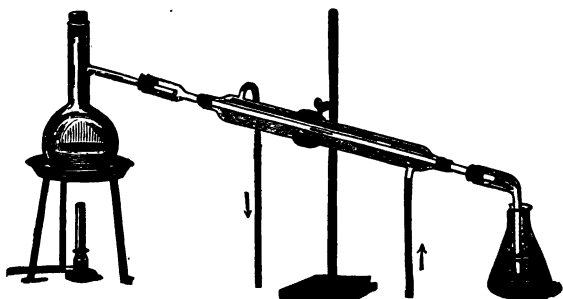
FIG. 38.

in the distilling flask and cooled to the ordinary temperature under the tap. The potassium bromide, coarsely powdered, is then added. The flask, which is closed with a cork, is fixed to the condenser and heated on the sand-bath. A sufficient quantity of water is poured into the receiver to close the end of the adapter. After a short time the liquid in the flask begins to boil and froth up, and the ethyl bromide, in the form of heavy drops of colourless liquid, distils and collects at the bottom of the receiver. If the liquid threatens to froth over, the flask must be raised from the sand-bath for a moment. The distillation is continued until no further drops of oil appear at the end of the condenser. As the ethyl bromide has a low boiling point

(38-39°), it is desirable to surround the receiver with ice during this operation. The distillate is now removed and poured into a separating funnel (Fig. 39), and the *lower layer* of ethyl bromide separated. The water is thrown away and the ethyl bromide poured back together with about an equal bulk of dilute sodium carbonate solution and shaken up. The ethyl bromide is withdrawn, as before, and again shaken up with water. Finally, it is carefully separated from the water and run into a dry distilling flask. The small quantity of water which remains, and renders the liquid turbid, is removed by adding a few small pieces of solid calcium chloride. The flask is corked and left to stand for some hours until the liquid becomes clear. A thermometer is inserted into the neck of the flask with the bulb just below the side tube. The flask is attached to a condenser and heated gently on the water-bath, so that the liquid distils at a moderate speed (2-3 drops a second). The temperature is noted and the portion boiling at 35-40° collected in a separate flask. This consists of ethyl bromide which may contain a little ether. Yield 75-80 grams.

Fig. 39.

$$C_2H_5OH + H_2SO_4 = C_2H_5.H.SO_4 + H_2O.$$

Alcohol.   Ethyl hydrogen sulphate.

$$C_2H_5.H.SO_4 + KBr = C_2H_5Br + KHSO_4.$$

Ethyl bromide.
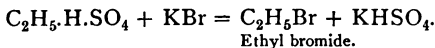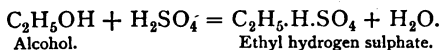
Properties—Colourless liquid ; b. p. 38·8° ; sp. gr. 1·47 at 15°.

Determination of Specific Gravity.—A simple method for determining the specific gravity of liquids is as follows : A pyknometer, or small glass bottle, is used of about 20 to 30 c.c. capacity, with narrow neck, upon which a mark is etched and which is closed by a ground glass stopper (Fig. 40).

The bottle is thoroughly cleaned and dried by warming and aspirating air through it, after which it is allowed to cool and weighed. It is then filled with the liquid, which is poured in

COHEN'S ADV. P. O. C.   E

through a funnel, the stem of which is drawn out so as to pass through the narrow neck. The bottle is placed in a mixture of snow or pounded ice and left a quarter to half an hour, until the contents have a temperature of 0°. The meniscus is now adjusted until it coincides with the mark on the neck of the bottle. If more liquid has to be added, this may be done from a small pipette with capillary delivery tube ; if some of the liquid has to be removed, a thin roll of filter paper may be inserted which will absorb it. The bottle is then stoppered, dried on the outside, left in the balance case for a quarter of an hour, and weighed. It is then emptied, cleaned, and dried, and filled with distilled water previously boiled. The water is cooled to 0°, the meniscus adjusted and the bottle weighed, the same process being repeated as that just described.

FIG. 40.

The following expression will give the specific gravity of the liquid at 0° compared with water at 0° :—

$$\Delta = \frac{w_3 - w_1}{w_2 - w_1}$$

Where w_1 = weight of empty bottle,
  w_2 =   „   bottle and water at 0°,
  w_3 =   „   bottle and liquid at 0° ;

or, if compared with water at 4°, the above number must be multiplied by the density of water at 0° = ·999873.

A very delicate and useful piece of apparatus, which is readily made with the blow-pipe, is Perkins's modification of Sprengel's specific gravity tube.[1] It is especially adapted for small quantities of liquid and for the more volatile ones. The apparatus (Fig. 41) consists of a U-tube to hold from 2 to 10 c.c., drawn out at each end into a fine capillary. The one capillary limb, a, is bent outwards and is furnished with a small bulb ; the other, b, is bent at a right angle with the first. On the limb a, between the bulb and the top of the U-tube a mark is etched. The

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[1] *Chem. Soc. J.*, xlv. p. 421,

tube is dried and weighed, and the liquid drawn in through the limb *b*, until it half fills the small bulb on the limb *a*. The apparatus is cooled in ice and water, and the meniscus adjusted to the mark on *a* by tilting the tube until the limb *b* has a horizontal position. To the end of this limb a piece of filter paper is applied, until the liquid sinks to the desired position in the
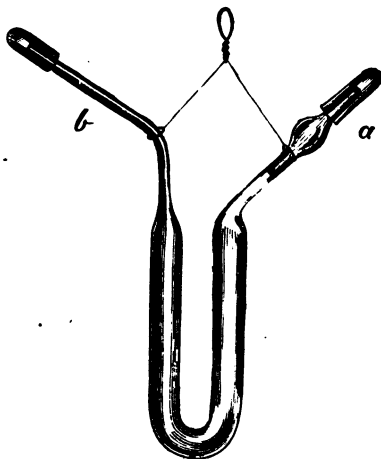
FIG. 41.

limb *a*. The **U**-tube is then brought to the vertical position, loose glass caps placed over the ends of the two limbs, the apparatus carefully dried, and allowed to stand and weighed. The operation is then repeated with distilled water.

Example—An experiment with ethyl bromide gave the following result :—

Weight of tube empty . . . . 6·242 grams

+ ethyl bromide at 0° . . 9·472 ,,

+ water at 0° . . . . . . 8·417 ,,

$$\Delta \frac{0^\circ}{4^\circ} = \cdot999873 \times \frac{3\cdot230}{2\cdot175} = 1\cdot485.$$

Determination of the Boiling-point.—A correct determination of the boiling-point of a liquid is made with a standard

E 2

thermometer, *i.e.*, one that has been calibrated, and the 0° and 100° points carefully determined. An ordinary thermometer corrected by a standard thermometer at Kew will serve equally well. Correction must also be made for barometric pressure. This is approximately ·043° for every 1 mm. below 760 (Landolt). A further correction is required for the thread of mercury, which may project above the vessel. For this correction the following formula may be used :—

$$N(T - t)·000154.$$

Where T = apparent temperature in degrees.

t = temperature of a second thermometer, the bulb of which is placed at half the length N above the vessel.

N = length of the mercury column in degrees from above the vessel to T.

·000154 = apparent expansion of mercury in glass.

This correction may be avoided by using short (Anschütz) thermometers, in which the mercury thread is entirely immersed in the vapour. A rough correction for points above 100° may be made by determining the boiling points of pure organic substances, such as naphthalene, 216·6°, &c.

PREPARATION 3.

Ether (Diethyl Ether, Diethyl Oxide), $(C_2H_5)_2O$

V. Cordus (1544); Boullay (1815), *Journ. Pharm.*, 1, 97; Williamson (1850), *Phil. Mag.* (3) 37, 350.

    150 grms. (80 c.c.) conc. sulphuric acid.
    85 „   (110 c.c.) absolute alcohol.

A distilling flask (½ litre) is fitted with a double-bored cork. Through one hole a thermometer is inserted, the bulb of which must be covered by the liquid in the flask and through the other a tap-funnel passes. The side-tube of the distilling flask is fixed by a cork into the upper end of a long condenser. An adapter is fitted to the lower end and passes through the neck of a flask, which is surrounded by ice. The apparatus is shown

in Fig. 42. The sulphuric acid and alcohol are cautiously mixed together in the distilling flask, which is then placed upon a sand-bath and attached to the condenser. The mixture is heated to 140° and alcohol is run in from the tap funnel at the same speed as the liquid distils (about three drops a second). The temperature must be kept constant at 140—145°. When about three the quantity of alcohol contained in the original mixture has been added and converted into ether, the distillation is stopped. The receiver now contains, in addition to ether, alcohol, water and sulphurous acid. The liquid is poured into
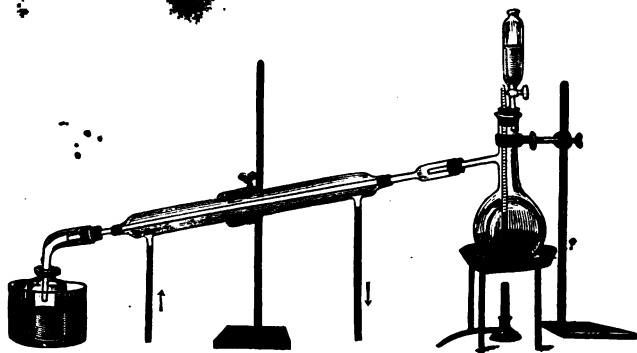

FIG. 42.

a large separating funnel and a small quantity (30—40 c.c.) of dilute caustic soda added and well shaken. After settling the caustic soda solution is drawn off below, and about the same quantity of a strong solution of common salt added, and the process of shaking and drawing off repeated. The ether, which is now free from sulphurous acid and from most of the alcohol, still contains water. It is therefore poured into a large dry distilling flask and some pieces of solid calcium chloride added. It is allowed to stand loosely corked over night. The distilling flask is now attached to a long condenser and heated on the water-bath. The ether, which distils, still contains traces of alcohol and water, which it obstinately retains and from which it can only be freed

by a further treatment with metallic sodium. A few very thin slices of sodium are dropped into the receiver and the vessel closed with a cork, through which an open calcium chloride tube is inserted to allow any hydrogen to escape and to prevent the entrance of moisture.

When the sodium produces no further action, the ether is decanted from the sodium residues into a distilling flask and distilled on the water-bath. A thermometer is placed in the neck of the flask to indicate the boiling point, which should be constant at 35°.

$$C_2H_5OH + H_2SO_4 = C_2H_5SO_4H + H_2O.$$
$$C_2H_5SO_4H + C_2H_5OH = C_2H_5.O.C_2H_5 + H_2SO_4.$$
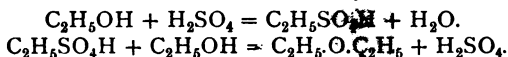
Properties.—Colourless, mobile liquid; b.p. 35°; sp.gr. ·720 at 15°; burns with a luminous flame; not miscible with water; 9 parts of water dissolve 1 part of ether, and 35 parts of ether dissolve 1 part of water at the ordinary temperature.

Commercial Ether is made from methylated spirit and contains alcohol, water, and other impurities, and for many
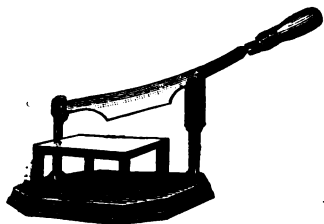
FIG. 43.
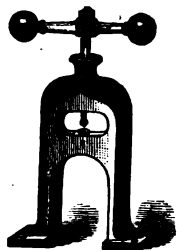
FIG. 44.

reactions requires to be purified. The above method of purification may be employed. The ether is first shaken with small quantities of salt solution then placed in contact with solid calcium chloride for several hours, and finally decanted and treated with metallic sodium. It is convenient to use a sodium knife (Fig. 43) or press (Fig. 44) for preparing the sodium. In the former the metal can be cut into very thin slices, and in the latter it is pressed into fine wire through a circular steel die.

It must be remembered that ether is highly inflammable, and also exceedingly volatile, and great care should be taken that no flame is in the neighbourhood of the liquid. It must on no account be distilled over the bare flame, but always from the water-bath, and then with a long well-cooled condenser. The distillation of large quantities should be avoided as far as possible. In such cases it is convenient to employ a distilling flask of moderate size (250 c.c.), and to add, as the liquid distils, a fresh supply of ether or ethereal liquid from a tap-funnel inserted through the neck of the flask, which can be done without interrupting the distillation.

PREPARATION 4.

Ethylene Bromide. $CH_2Br.CH_2Br.$

Balard (1826), *Ann. Ch. Phys.* (2) 32, 375 ; Erlenmeyer, Bunte (1873), *Ann.*, 168, 64.

> 25 grms. (30 c.c.) absolute alcohol.
> 150   „   (80 c.c.) conc. sulphuric acid.
> 200   „   (65 c.c.) bromine (which must be measured out in the fume-cupboard).
> 300   „   of a mixture of 100 grms. (124 c.c.) alcohol and 200 grms. (108 c.c.) conc. sulphuric acid.

Fit up an apparatus as shown in Fig. 45. It consists of a round flask (2 litres), which is furnished with a double-bored cork. A tap-funnel is inserted through one hole and a delivery tube through the other, by which it is connected with two wash-bottles with safety tubes. A useful form of wash-bottle is that shown in Fig. 45 and in section at *a*. Otherwise a three-necked Woulff bottle will serve, with a long tube inserted through the central neck. The wash-bottles are one-third filled with caustic soda solution. The two ordinary wash-bottles standing in the trough of water contain the bromine. The first contains about 50 c.c. of bromine and 1 c.c. of water and the second about 15 c.c. of bromine and 1 c.c. of water. The latter is attached to a wide **U** tube or cylinder containing pieces of soda-lime. If a cylinder is used a layer of glass fragments or marbles should

form a layer round the orifice of the inlet tube with the soda-lime above.

The joints being tight, the mixture of 25 grams of alcohol and 150 grams of sulphuric acid is run into the large flask and heated with a small flame on the sand-bath until a steady stream of gas is evolved. When this occurs the mixture of alcohol and sulphuric acid is dropped in slowly from the tap-funnel. It is important to moderate the temperature to prevent excessive frothing and the separation of carbon, which, however, cannot altogether be avoided. A considerable quantity of sulphur dioxide which is evolved with the ethylene
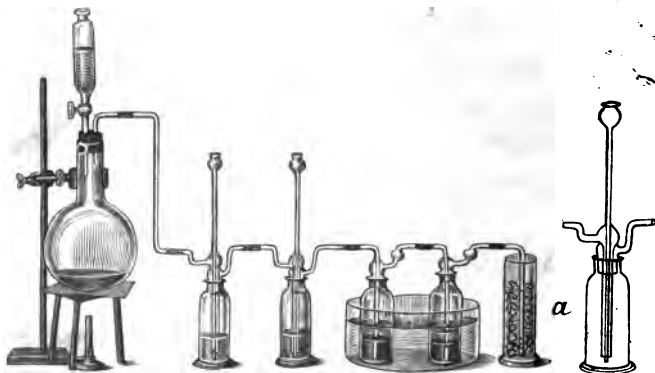

FIG 45.

is removed by the caustic soda in the wash-bottles. If the water surrounding the bromine bottles becomes warm, small lumps of ice should be thrown in. The caustic soda should be occasionally renewed, otherwise sulphur dioxide may pass into the bromine and reduce it to hydrobromic acid. If the pressure in the apparatus causes a back rush of bubbles through the tap-funnel attached to the flask, the difficulty is met by inserting the stopper in the tap-funnel. After a few hours the bromine in both vessels is decolourised or at least changes to a straw colour. The crude ethylene bromide is removed and shaken with dilute caustic soda solution, then with water, separated from the aqueous layer and dehydrated

over small pieces of calcium chloride. It is decanted or filtered from the calcium chloride and distilled. The distillate is collected at 130—132°. The yield is nearly equal to the weight of bromine taken.

$$C_2H_5(OH) - H_2O = C_2H_4$$
$$C_2H_4 + Br_2 = C_2H_4Br_2$$
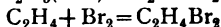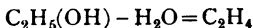
Properties. Colourless liquid, which solidifies, at 0° to a crystalline mass and melts at 9°; b. p. 131·5°; sp.gr. 2·17 at 20°.

Reaction. Attach a 100 c.c. flask to a short upright condenser and to the upper end of the condenser attach a vertical delivery tube, dipping into an ammoniacal cuprous chloride [1] solution. Pour 2–3 c.c. of ethylene bromide into the flask with 4 times its volume of strong methyl alcoholic potash, which is prepared by boiling methyl alcohol with excess of caustic potash on the water-bath with upright condenser. On gently heating, a rapid evolution of acetylene occurs and the characteristic brown copper compound $(C_2H_2Cu_2H_2O)$ is precipitated from the cuprous chloride solution.

$$C_2H_4Br_2 + 2KOH = C_2H_2 + 2KBr + 2H_2O$$
Acetylene
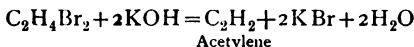
PREPARATION 5.

Acetaldehyde, $CH_3.CO.H$

Liebig (1835), *Ann.*, 14, 133; Staedeler (1859), *J. Prakt. Chem.* (1) 76, 54.

> 100 grms. potassium bichromate
> 420 c.c. water.

A mixture of 100 grms. (125 c.c.) absolute alcohol and 140 grms. (75 c.c.) conc. sulphuric acid.

100 c.c. methylated ether, which has been left to stand over solid calcium chloride for a few hours, and then distilled off from the water-bath.

A round flask (1½ litre) is provided with a double-bored cork.

[1] *Ammoniacal cuprous chloride* is made as follows: Boil up copper oxide and metallic copper with conc. hydrochloric acid for a short time until the liquid is nearly colourless, and pour the liquid into water. The white cuprous chloride is washed once or twice by decantation and dissolved in a strong solution of ammonium chloride. When required a little ammonia is added sufficient to give a clear blue solution.

A bent tube, which passes through one hole, connects the flask
with a condenser and receiver. A tap-funnel is inserted through
the other hole. The flask is placed upon a sand-bath, and the
receiver is cooled in ice. It is important that the cork of the
flask should be tight, as a small leak will considerably diminish
the yield. The potassium bichromate in small pieces and the
420 c.c. of water are placed in the flask and gently warmed.
The flame is then removed, and the mixture of alcohol and
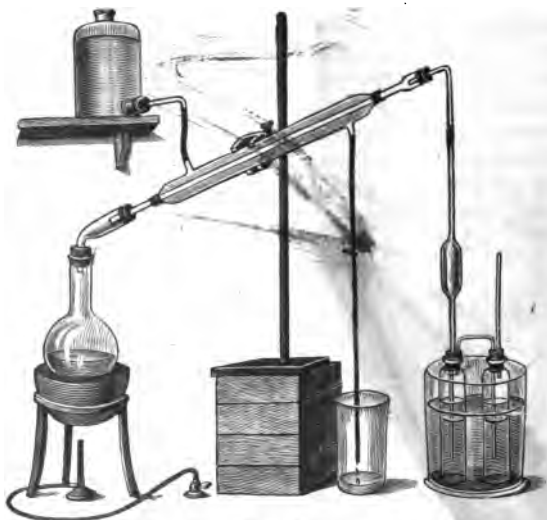
FIG. 46.

sulphuric acid, which may be used warm, is slowly added from
the tap-funnel. The flask is occasionally shaken. A consider-
able rise of temperature occurs and the liquid darkens, whilst
aldehyde, with a little water and alcohol, distils. When the
mixture has all been added, the flask is heated on the sand-bath
until all the aldehyde has distilled (about 150 c.c.), which may
be determined by removing the cork from the flask and noticing
if the smell of aldehyde is still perceptible. The distillate is now
redistilled on the water-bath in the apparatus shown in Fig. 46.

The flask is attached to an upright condenser in which the water is kept at a temperature of 30—35°. Alcohol and aqueous vapour condense in the condenser; the aldehyde, on the other hand, passes by a tube attached to a 100 c.c. pipette into two narrow (100 c.c.) cylinders, one-third filled with the dry ether, and cooled in ice-water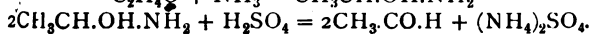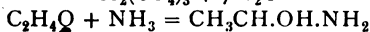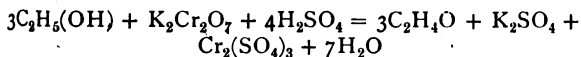. The aldehyde readily dissolves in the ether and is rapidly absorbed. If the ethereal solution is now saturated with dry ammonia gas, the whole of the aldehyde separates out in the form of colour-less crystals of aldehyde-ammonia, $CH_3.CH.OH.NH_2$. The apparatus for preparing the dry ammonia is shown in Fig. 47. The flask containing strong ammonia solution is heated by a *small* flame, when the gas is readily evolved and passes up the tower, which is filled with soda-lime or quicklime. The ethereal solution is saturated with the gas, and is then allowed to stand for an hour.

FIG. 47.

The ether is then decanted from the crystals, which are drained at the filter-pump, washed with a little ether, and finally dried in the air on filter-paper. Yield of aldehyde-ammonia, 25—30 grams.

From the aldehyde-ammonia thus obtained, pure aldehyde may be prepared. The crystals are dissolved in an equal weight of water and distilled on the water-bath with a mixture of $1\frac{1}{2}$ parts of concentrated sulphuric acid and 2 parts of water, the receiver being well cooled in ice. The temperature of the water-bath is gradually raised until the water begins to boil, and the distillation is then interrupted. The distillate is de-hydrated over an equal bulk of calcium chloride, from which it is distilled in the water-bath, heated to 30°. The anhydrous aldehyde is kept in a well-stoppered bottle.

$$3C_2H_5(OH) + K_2Cr_2O_7 + 4H_2SO_4 = 3C_2H_4O + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$
$$C_2H_4O + NH_3 = CH_3CH.OH.NH_2$$
$$2CH_3.CH.OH.NH_2 + H_2SO_4 = 2CH_3.CO.H + (NH_4)_2SO_4.$$

Properties.—Colourless liquid with a distinctive smell ; b. p. 21° ; sp. gr. ·807 at 0° ; soluble in water, alcohol and ether.

Reactions.—Acetaldehyde and many of the aliphatic aldehydes are characterised by the following reactions :—

1. Prepare a little ammonio-silver nitrate by adding dilute ammonia drop by drop to silver nitrate solution until the precipitate just dissolves. Add to a third of a test-tube full of the ammonia-silver nitrate solution about 1 c.c. of aldehyde, and place it in a beaker of hot water. A mirror of metallic silver is deposited. $Ag_2O + C_2H_4O = Ag_2 + C_2H_4O_2$ (acetic acid).

2. To 1 c.c. of aldehyde add 2-3 times its volume of a cold *saturated* solution of sodium bisulphite and shake up. The additive compound, $CH_3CH.OH.SO_3Na$, crystallises out on standing. A crystal of the substance introduced into the liquid will hasten its formation. The bisulphite solution is prepared either by dissolving sodium metabisulphite in water, or by passing sulphur dioxide into soda crystals covered with a layer of water. It forms an apple-green solution, smelling strongly of sulphur dioxide. The sulphur dioxide is conveniently obtained by dropping concentrated sulphuric acid on to solid sodium sulphite.

3. A solution of magenta decolourised by sulphur dioxide becomes violet on the addition of a drop of aldehyde (Schiff). Prepare a weak solution of magenta by dissolving a crystal in half a test-tube of water and bubbling in sulphur dioxide until the colour disappears. Now add a few drops of aldehyde.

4. Boil a few drops of aldehyde with 1—2 c.c. of caustic potash solution. The liquid becomes yellow and a brown resinous precipitate is formed.

5. Add a drop or two of concentrated sulphuric acid to 1 c.c. of aldehyde. The mixture becomes hot in consequence of the aldehyde undergoing polymerisation to paraldehyde $(C_2H_4O)_3$. b. p. 124°, which separates as an oil on adding water.

Methyl Alcohol. $CH_3.OH$

Commercial methyl alcohol is obtained by purifying wood spirit. It often contains a little acetone, which may be detected by the iodoform reaction, see p.44. It may, if necessary, be purified by boiling it, using an upright condenser, with 3—4 per cent. of solid

caustic potash on the water-bath, and then distilling. It is freed from water by standing for twenty-four hours in a flask one-third filled with freshly-burnt quicklime, and re-distilling from the water-bath with a thermometer.

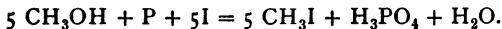*Properties.*—Colourless liquid ; b. p. 66—67° ; sp. gr. ·796 at 20°.

PREPARATION 6.

Methyl Iodide (Iodomethane), CH_3I

Dumas and Peligot (1835), *Ann.*, 15, 20.

> 18 grms. methyl alcohol
> 5 „ red phosphorus
> 50 „ iodine.

Attach a flask (250 c.c.), to an upright condenser, and bring into it the methyl alcohol and red phosphorus. Add the iodine gradually by detaching the flask for a moment from the condenser. A considerable evolution of heat occurs. When the iodine has been added the flask is left attached to the condenser over night, and the contents then distilled from the water-bath using a similar apparatus to that of Fig. 38, p. 48. The distillate is shaken up with dilute caustic soda in a separating funnel, to remove iodine and hydriodic acid. If sufficient caustic soda has been used the lower layer of methyl iodide will be colourless. Separate the methyl iodide, add a few pieces of solid calcium chloride, and after standing until clear, distil from the water-bath with thermometer. Yield 45 grams.

$$5 CH_3OH + P + 5I = 5 CH_3I + H_3PO_4 + H_2O.$$

Properties.—Colourless, highly refractive liquid ; b. p. 44° ; sp. gr. 2·27 at 15°.

Amyl Alcohol. $C_5H_{11}.OH.$

Commercial amyl alcohol is contained in fusel oil from fermentation and consists mainly of isobutyl carbinol together with about 13 per cent. of methyl ethyl carbin-carbinol, which renders the liquid optically active. It turns the plane of polarisation to the left (see p. 104).

Properties.—Colourless, highly refractive liquid with a burning taste and penetrating smell ; b. p. 131—132° sp. gr, ·8113 at 19°; dissolves in 39 parts of water at 16·5°.

PREPARATION 7.

Amyl Nitrite. $C_5H_{11}O.NO.$

Balard, Guthrie *Quart J. C. S.*, 11, 245 ; Rennard (1874), *Jahresb.*, 352.

> 30 grms. amyl alcohol.
> 30 „ sodium nitrite (finely powdered).
> 18 „ conc. sulphuric acid. (/ 5+)

The amyl alcohol and sodium nitrite are mixed in a flask (500 c.c.), and whilst the mixture is cooled in ice-water, the conc. sulphuric acid is added drop by drop from a funnel with constant shaking. Towards the end of the process a more vigorous reaction sets in, when care must be taken to add the sulphuric acid more slowly. When the whole of the acid has been added, the top layer of amyl nitrite is decanted into a separating-funnel. A little water is then added to the residue and, after shaking, a further quantity of amyl nitrite separates and is decanted as before. The whole of the nitrite is then separated from any water it may contain, dehydrated over calcium chloride and distilled. The liquid boiling at 95—100° is collected separately. Yield, 30—35 grams.

$$C_5H_{11}OH + NaNO_2 + H_2SO_4 = C_5H_{11}O.NO + NaHSO_4 + H_2O.$$
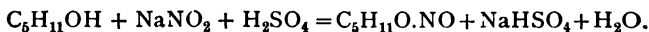
Properties.—Yellow-green liquid with a peculiar penetrating and sweet smell, which, on inhaling, causes a rush of blood to the head ; b. p. 96° ; sp. gr. ·902.

Acetone (Dimethyl ketone) $CH_3.CO.CH_3$

Commercial acetone is obtained from the products of the distillation of wood. To purify it, it is shaken with a saturated solution of sodium bisulphite (see Reaction 2, p. 60). The crystalline mass $C_3H_6ONaHSO_3$, is filtered and well drained and then distilled with sodium carbonate solution. The distillate is dehydrated over solid calcium chloride and finally distilled.

Properties. Colourless liquid with a pleasant colour ; b.p 56·3° ; sp. gr. ·792 at 15° ; soluble in water.

Reactions. 1. Acetone gives the *iodoform reaction* like ethyl alcohol. 2. Dissolve a few crystals of p. bromophenylhydrazine in a few drops of glacial acetic acid, dilute with about 1 c.c. of water and add a drop of acetone. The bromophenylhydrazone of acetone separates out in needles.

PREPARATION 8.

Chloroform (Trichloromethane) CHCl₃

Liebig (1831), *Pogg. Ann.*, 23, 444 ; Dumas (1834), *Ann. Chim. Phys.*, 56, 115.

> 200 grms. bleaching powder (fresh).
> 800 c.c. water.
> 40 grms. (50 c.c.) acetone.

A large round flask (4 litres) is fitted with a cork, through which a bent tube passes connecting the flask with a long condenser and receiver. The flask is placed upon a large sand-bath. Grind the bleaching powder into a paste with 400 c.c. of water and rinse it into the flask with the remaining 400 c.c. Add the acetone and attach the flask to the condenser. Heat cautiously until the reaction sets in, which is indicated by the frothing of the liquid. Remove the flame for a time, and when the reaction has moderated, boil the contents until no more chloroform distils. This is easily determined by collecting the distillate in a test-tube and observing if any drops of heavy liquid are present. The distillate is shaken with dilute caustic soda solution in a separating funnel and the lower layer of chloroform run into a distilling flask. A few pieces of solid calcium chloride are added and left until the liquid is clear, when it is distilled from the water-bath with a thermometer inserted into the neck of the flask. Yield about 40 grams.

The bleaching powder acts as though it consisted of a compound of calcium hydrate and chlorine, and the process probably occurs in two stages.

1. $CH_3COCH_3 + 3Cl_2 = CH_3.CO.CCl_3 + 3HCl.$
2. $2CH_3.CO.CCl_3 + Ca(OH)_2 = (CH_3.COO)_2Ca + 2CHCl_3.$
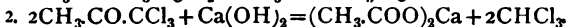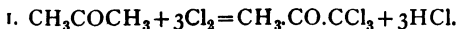
Trichloracetone is first formed which is then decomposed by the lime into calcium acetate and chloroform.

Properties.—Colourless liquid possessing a sweet smell, b. p. 61—62°; sp. gr. 1·525 at 0°; very slightly soluble in water; non-inflammable. As chloroform slowly decomposes in presence of air and sunlight into phosgene, it is usual to add a little alcohol to the commercial product, which arrests the change. Pure chloroform is neutral to litmus, has no action on silver nitrate solution and does not discolour concentrated sulphuric acid, when shaken with it for an hour or left for a day.

Reactions.—1. Heat a few drops with double its volume of methyl alcoholic potash. On the addition of water a clear solution is obtained. Potassium formate and chloride are formed. $CHCl_3 + 4KOH = 3KCl + HCO.OK + 2H_2O$.

2. Bring into a test-tube two drops of chloroform, one drop of aniline and 1 c.c. of alcoholic potash and warm in the fume cupboard. Note the intolerable smell of phenyl carbamine (carbamine reaction) $CHCl_3 + C_6H_5NH_2 + 3KOH = C_6H_5NC + 3KCl + 3H_2O$.

<div align="center">

PREPARATION 9.

$$CH_3$$
$$|$$
Acetoxime, $C:NOH$
$$|$$
$$CH_3$$
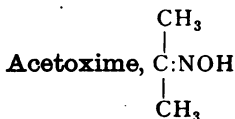
V. Meyer, Fanin (1882), *Ber.*, 15, 1324.

</div>

5 grms. hydroxylamine hydrochloride in 10 c.c. water
3   „   caustic soda in 10 c.c. water
6   „   acetone.

Add the acetone to the mixture of the hydroxylamine hydrochloride and caustic soda in a small flask. The flask is then corked and left for twenty-four hours during which the crystalline oxime separates. The presence of any free hydroxylamine is then tested in a few drops of the liquid with Fehling's solution, or by merely adding a drop or two of copper sulphate, then a sufficient quantity of caustic soda to produce a clear blue solution and warming. An orange red precipitate of cuprous

oxide indicates uncombined hydroxylamine. If no free hydroxylamine is present, the liquid is shaken up with an equal volume of ether, in which the acetoxime dissolves. The ethereal solution is separated and the process repeated twice with fresh ether. The united ethereal extract is filtered, if necessary, through a dry filter into a distilling flask. The greater part of the ether is distilled off on the water-bath. The remaining liquid is poured into a glass basin and the rest of the ether left to evaporate in the air, the last traces being removed by heating for a few minutes on the water-bath. The acetoxime separates out on cooling in colourless needles. It is dried on a porous plate and recrystallised from a little petroleum spirit m.p. 61—62°. Yield 4—5 grams.

$$CH_3.CO.CH_3 + NH_2OH.HCl + NaOH$$
$$= CH_3.C:NOH.CH_3 + NaCl + 2H_2O$$
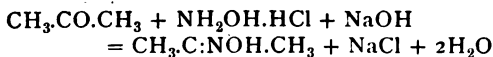
Properties.—Colourless needles ; m. p. 61—62°.

Reaction.—Boil a small quantity for a few minutes with dilute hydrochloric acid, and test with Fehling's solution. The oxime is decomposed into acetone and hydroxylamine,

$$CH_3.C(NOH)CH_3 + H_2O$$
$$= CH_3.CO.CH_3 + NH_2OH.$$
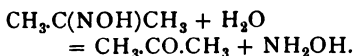
Melting-Point Determination.—For this purpose the following apparatus is used (Fig 48). A small sample of finely powdered substance, which has been carefully dried, is introduced into a capillary tube of about 1 mm. inside diameter sealed at one end. The tube is made from a test-tube by rotating it in the flame until the glass softens, and then quickly drawing it out. The long capillary is then broken into lengths of about 7 c.m. (2½ in.), each of

FIG. 48.

which is sealed at one end. To introduce the substance, it is convenient to scoop up the powder off a watch glass with the open end. By tapping the closed end on the bench, the powder is shaken down. The quantity introduced should occupy a length of about 4 mm. when tightly

COHEN'S ADV. P. O. C.   F

packed. The tube is attached to a thermometer so that the substance is level with the bulb. The attachment may be made by a narrow rubber ring or by simply moistening the side of the capillary with the thermometer bulb, which has been dipped in the sulphuric acid bath, and then pressing it against the thermometer stem. The thermometer passes through a cork inserted into a large test-tube, filled about 4 cm. ($1\frac{1}{2}$ in.) in depth with concentrated sulphuric acid. A second hole in the cork admits a glass stirrer, which is kept in position by a short glass tube in which it slides. The test-tube is clamped on a ring of wire-gauze and is heated very gradually by a small flame. When a certain temperature is reached the substance, if pure, melts suddenly within one or two degrees. When approaching the melting point, it is desirable to remove the flame or turn it very low so that the rise of temperature is very gradual. If the liquefaction is protracted, it is an indication that the substance is not pure. The melting-point, obtained in this way, to be quite accurate, must be corrected for the temperature of the thread of mercury outside the liquid, the same formula being used as in the correction for the boiling point (see p. 52). When the acid becomes discoloured, a crystal of potassium nitrate will remove the colour on warming.

Acetic Acid, $CH_3.CO.OH$.

Commercial acetic acid is manufactured from pyroligneous acid obtained in the destructive distillation of wood. The latter is neutralised with lime, and separated by distillation from wood-spirit and acetone. The crude calcium acetate, which has a dark colour, is then distilled with the requisite quantity of concentrated hydrochloric acid. Anhydrous or glacial acetic acid is obtained by distilling fused sodium acetate with concentrated sulphuric acid.

Properties.—Colourless liquid with pungent smell ; b. p. 119° ; m. p. 16·7° ; sp. gr. 1·055 at 15°. It should not decolourise a solution of permanganate. The vapour of the boiling acid is inflammable.

Reactions.—Add a few drops of alcohol to the same quantity of acetic acid, and an equal volume of concentrated sulphuric. Warm gently and notice the fruity smell of ethyl acetate.

Neutralise a few drops of acetic acid by adding excess of ammonia and boiling until neutral. Let cool and add a drop of ferric chloride. The red colour of ferric acetate is produced. On boiling, basic ferric acetate is precipitated.

PREPARATION 10.

Acetyl Chloride, $CH_3.CO.Cl.$

Gerhardt (1853), *Ann. Ch. Phys.* (3) 37, 285 ; Béchamp (1855), *Compt. rend.*, 40, 944, and (1856), 42, 224.

> 50 grms. glacial acetic acid.
> 40 ,, phosphorus trichloride.

Fit up the apparatus shown in Fig. 49. It consists of a distilling flask (250 c.c.), which is attached to a condenser. A second distilling flask serves as receiver, the side tube being attached
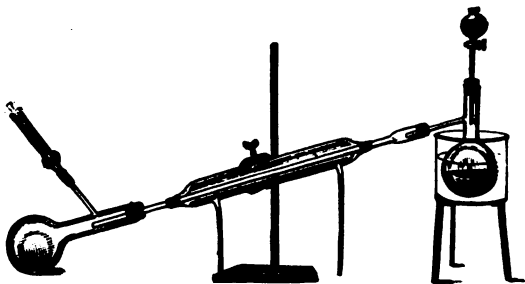
FIG 49

to a calcium chloride tube. The distilling vessel is provided with a cork, through which a tap-funnel is inserted. The flask is cooled in cold water in the water-bath (outlined in Fig. 49), whilst the phosphorus trichloride is slowly run in from the tap-funnel.* When the phosphorus chloride has been added, the water in the water-bath is warmed to 40°—50°, until the evolution of hydrochloric acid gas, which at first is very rapid, begins to abate. The water-bath is then heated to boiling, until nothing further distils. The distillate is now redistilled as

F 2

before, but with a thermometer, and the distillate collected at the boiling point of acetyl chloride (53°—56°). Yield 45 grams.

$$3CH_3COOH + 2PCl_3 = 3CH_3.COCl + P_2O_3 + 3HCl.$$
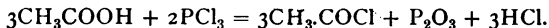
Properties.—Colourless liquid with a pungent smell; it fumes in contact with moist air; b. p. 55°; sp. gr. 1·105 at 20°.

Reactions. 1.—Add a few drops of acetyl chloride to about 5 c.c. of water in a test-tube. The acetyl chloride sinks to the bottom of the test-tube, but on shaking, rapidly dissolves, and heat is evolved. The acetyl chloride is converted into acetic acid and hydrochloric acid.

$$CH_3.COCl + H_2O = CH_3.CO.OH + HCl$$
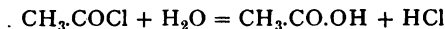
2. To about 1 c.c. of ethyl alcohol in a test-tube, add 1 c.c. of acetyl chloride drop by drop, cooling under the tap. Then add about 1 c.c. of a solution of common salt. Ethyl acetate separates out on the surface of the liquid, distinguished by its fragrant smell.

$$CH_3.COCl + C_2H_5OH = CH_3.CO.OC_2H_5 + HCl.$$

3. Add two drops of acetyl chloride to a drop of aniline. A vigorous action occurs, and a solid separates. This is acetanilide, and may be obtained in larger crystals by dissolving in boiling water and cooling slowly.

$$CH_3.COCl + C_6H_5NH_2 = C_6H_4NH.CO.CH_3 + HCl.$$

PREPARATION 11.

Acetic Anhydride (Diacetyl Oxide). $\begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\Big\rangle O.$

Gerhardt (1853), *Ann. Ch. Phys.* (3) 37, 311.

> 55 grms. sodium acetate (fused).
> 40 „ acetyl chloride.

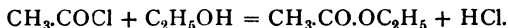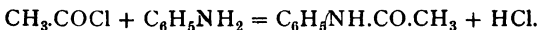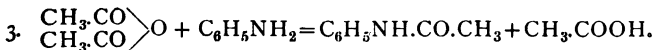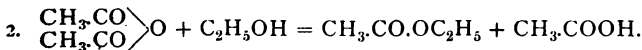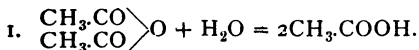A retort (250 c.c.) is attached to a short condenser and receiver, which is furnished, as in the previous preparation, with a calcium chloride tube. The tubulus of the retort is closed by

a cork, through which a tap-funnel is fixed. The fused sodium acetate is prepared by fusing crystallised sodium acetate, $(CH_3.COONa + 3H_2O)$. The sodium acetate (100 grams) is placed in a shallow tin and heated over a Bunsen burner. It first melts in the water of crystallisation, after which it becomes solid, and finally melts again as the temperature rises. When completely melted it is allowed to cool, powdered, and introduced into the retort. The acetyl chloride is gradually added through the tap-funnel, the retort being cooled in water.* When the acetyl chloride has been added, the contents of the retort are well stirred by means of a thick glass rod pushed through the tubulus. The retort is now closed by an ordinary cork or stopper, and heated over a small flame, which should be moved about to prevent the retort cracking. When nothing further distils, the retort is allowed to cool somewhat, and the distillate poured back and redistilled. Finally it is distilled from a distilling flask with a thermometer, and collected at 130—140°. Yield 40 grams.

$$CH_3COCl + CH_3.CO.ONa = (CH_3.CO)_2O + NaCl.$$

Properties—Colourless liquid with an irritating smell ; b.p. 138° ; sp. gr. 1·08 at 15°.

Reactions—Repeat the three experiments described under acetyl chloride. The result is the same in each case ; but as the acetic anhydride reacts less readily than acetyl chloride, the mixture requires to be warmed.

1. $\begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\Big\rangle O + H_2O = 2CH_3.COOH.$

2. $\begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\Big\rangle O + C_2H_5OH = CH_3.CO.OC_2H_5 + CH_3.COOH.$

3. $\begin{matrix} CH_3.CO \\ CH_3.CO \end{matrix}\Big\rangle O + C_6H_5NH_2 = C_6H_5NH.CO.CH_3 + CH_3.COOH.$

In Reaction 2, combination is not complete, even on boiling, and a little dilute caustic soda must be added to decompose the unchanged acetic anhydride. In Reaction 3, the product remains liquid until water is added, when it becomes solid, and on heating dissolves.

PREPARATION 12.

Acetamide. $CH_3.CO.NH_2$.

Hofmann (1882), *Ber.*, 15, 981.

100 grms. ammonium acetate.

Acetamide may be obtained by simply distilling solid ammonium acetate from a distilling flask provided with a thermometer, using for a condenser a straight, wide tube. (See Fig. 50.) A considerable quantity of ammonia, water, and acetic acid distil, and when the temperature passes 180° the distillate solidifies, and consists mainly of acetamide. The
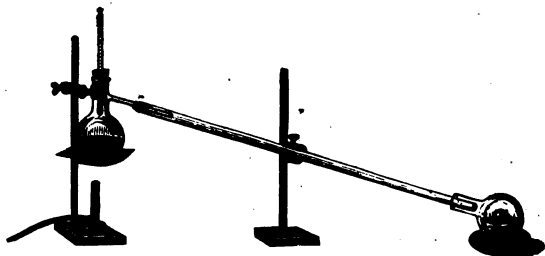
FIG. 50.

yield is, however, small. A better result is obtained by first heating the ammonium acetate for five to six hours in sealed tubes to 200°. The ammonium acetate may be prepared by adding to 70 grms. glacial acetic acid, warmed in a basin on the water-bath, about 80 grms. powdered ammonium carbonate until the acid is neutralised, which is recognised by diluting a sample with a little water, and testing with litmus. Two tubes are made from the usual thick-walled tubing (see p. 22). These are gently warmed, and the melted acetate then poured in until they are rather less than half full. They are then sealed in the usual way. After heating, the tubes contain a clear, oily-looking liquid, which consists of an aqueous solution of acetamide, together with some unchanged acetate. The contents are poured into a distilling flask and distilled with a straight tube as condenser, and the portion boiling above 180° collected in a

small beaker. This distillate, on standing, almost completely solidifies to a colourless crystalline mass. It is freed from mother-liquor by spreading on a porous plate, and purified by a second distillation. The acetamide has then a nearly constant boiling-point. Yield, about 40 grams.

$$CH_3.CO.ONH_4 = CH_3.CONH_2 + H_2O.$$
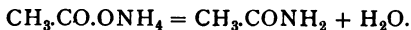
Properties.—Colourless, rhombohedral crystals, having a peculiar smell of mice. This is due to impurity, which may be removed by recrystallising from benzene ; m.p. 82° ; b.p. 222° ; easily soluble in water and alcohol.

Reaction.—1. Boil a small quantity of acetamide with caustic soda solution. Ammonia is evolved, and sodium acetate is found in solution, $CH_3.CONH_2 + NaOH = CH_3.CO.ONa + NH_3.$

PREPARATION 13.

Acetonitrile (Methyl cyanide), $CH_3.CN$

Dumas, Malaguti and Leblanc (1848), *Ann.*, 64, 332.

> 10 grms. acetamide
> ·15 „   phosphorus pentoxide.

The phosphorus pentoxide is introduced into a small distilling flask (200 c.c.) attached to a short condenser. As the pentoxide absorbs moisture rapidly and becomes sticky, it is convenient to push the neck of the distilling flask through a cork which fits the phosphorus pentoxide bottle, and then to shake in the oxide until the required weight is obtained. The powdered acetamide is immediately introduced and shaken up, and the mixture distilled over a small flame, which is constantly moved about. Add to the distillate about half its volume of water, and then solid potassium carbonate, until no more dissolves. The upper layer of liquid, which consists of methyl cyanide, is separated and distilled over a little fresh phosphorus pentoxide with thermometer. Yield, about 5 grams.

$$CH_3.CO.NH_2 - H_2O = CH_3CN.$$
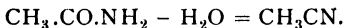
Properties.—Colourless liquid with peculiar smell ; b. p. 82°.
Reaction.—Boil a few grams of the acetonitrile with three

times its weight of a mixture of 2 vols. water and 3 vols. concentrated sulphuric acid for an hour with a long upright tube or air-condenser. Distil a few c.c. of liquid, and test the distillate for acetic acid, $2CH_3.CN + H_2SO_4 + 4H_2O = 2CH_3.COOH + (NH_4)_2SO_4$.

PREPARATION 14.

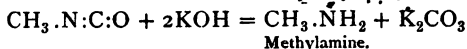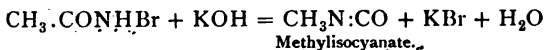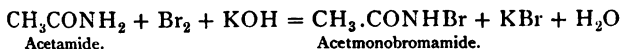### Methylamine Hydrochloride, $CH_3.NH_2.HCl$.

Würtz (1848), *Compt. rend.*, 28, 223 ; Hofmann (1882), *Ber.*, 14, 2725, and (1883), *Ber.*, 15, 407 and 762.

> 20 grms. acetamide
> 54 „ (18 c.c.) bromine
> 56 „ caustic potash.

The dry acetamide and bromine are mixed in a flask ($\frac{1}{2}$ litre), and whilst the mixture is cooled in water, a 10 per cent. solution of caustic potash (about 20 grams KOH) is added, until the dark brown liquid changes to a deep yellow colour. The solution, which now contains potassium bromide and acetmonobromamide, is slowly added from a tap-funnel inserted, together with a thermometer, into the neck of a distilling flask (1 litre). The flask contains a concentrated solution of caustic potash (56 grams in 100 c.c. of water), heated to 60—70°. Heat is evolved, and care must be taken that the rise of temperature does not greatly exceed the above limits. The reaction goes on quietly, and the yellow solution is gradually decolourised. The mixture is then digested for a short time at the above temperature until the yellow colour completely disappears. A few bits of broken pot are now introduced into the flask, which is closed with an ordinary cork, and the liquid distilled over wire-gauze. The vapours of methylamine and ammonia, which are cooled, are passed by means of a bent adapter, attached to the end of the condenser, into dilute hydrochloric acid contained in the receiver. Care must be taken that the adapter does not dip too far into the acid, or liquid may be sucked back into the condenser and distilling flask. When the distillate is no longer alkaline, and consequently all the methylamine has been driven over, the hydrochloric acid solution is evaporated to dryness on

the water-bath, and the colourless crystalline residue extracted repeatedly with small quantities of absolute alcohol, which dissolves out the methylamine salt from the ammonium chloride. From the hot alcoholic solution foliated crystals separate out on cooling.

$$CH_3CONH_2 + Br_2 + KOH = CH_3.CONHBr + KBr + H_2O$$
Acetamide.   Acetmonobromamide.

$$CH_3.CONHBr + KOH = CH_3N:CO + KBr + H_2O$$
Methylisocyanate.

$$CH_3.N:C:O + 2KOH = CH_3.NH_2 + K_2CO_3$$
Methylamine.

Properties.—Large deliquescent tablets, which melt at 200°, and sublime above 220°, with slight decomposition. The base is liberated on warming with caustic soda, as an inflammable gas with strong ammoniacal smell.

PREPARATION 15.

Ethyl Acetate (Acetic Ether), $CH_3.CO.OC_2H_5$.

Scheele (1782), *Chemical Essays*, 307 ; Frankland, Duppa (1865), *Phil. Trans.*, 156, 37 ; Pabst (1880), *Bull. Soc. Chim.*, 33, 350.

> 50 c.c. conc. sulphuric acid.
> 50 c.c. absolute alcohol.[1]

Mixture of equal volumes of glacial acetic acid (100 c.c.) and absolute alcohol (100 c.c.).

A distilling flask (½ litre) is attached to a condenser and receiver. The flask is provided with a cork, through which a separating funnel is inserted. The mixture of 50 c.c. of concentrated sulphuric acid and 50 c.c. of absolute alcohol is poured into the flask, which is then heated in a bath of paraffin wax or fusible metal[2] to 140°, and kept at this temperature. The mixture of equal volumes of acetic acid and alcohol is

[1] *Methyl acetate* may be made in precisely the same way, using methyl alcohol. The product is then fractionated and collected at 57—63°.
[2] A fusible metal bath has the advantage over an oil-bath of neither smelling nor being liable to catch fire. It is made by melting in a small cooking pan one part of lead and two parts of bismuth. This alloy is fluid above 120°.

now added, drop by drop, from the tap-funnel at the speed at which the liquid distils, as in the preparation of ether (p. 52). When all the mixture has been added, the distillate, which contains the ester, and also acetic acid, alcohol, ether, and sulphurous acid, is shaken in a separating funnel with a strong solution of sodium carbonate (50 c.c.) until the upper layer of ethyl acetate ceases to redden blue litmus. The lower layer is removed as completely as possible, and a strong solution of calcium chloride (50 grams in 50 c.c. of water) added, and the shaking repeated. The lower layer of calcium chloride is run off, and the ethyl acetate carefully decanted from the mouth of the funnel into a dry distilling flask. A few pieces of solid calcium chloride are added, and, after standing over night, the ethyl acetate is distilled from the water-bath with a thermometer in the neck of the flask. The portion distilling below 74° contains ether, that boiling at 74—79° is mainly ethyl acetate, and is separately collected. Yield, 80 per cent. of the theory.

$$C_2H_5(OH) + H_2SO_4 = C_2H_5.H.SO_4 + H_2O.$$
$$C_2H_5HSO_4 + CH_3.CO.OH = CH_3.COOC_2H_5 + H_2SO_4.$$
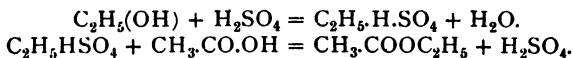
Properties.—Colourless liquid, with an agreeable fruity smell ; b. p. 77° ; sp. gr. ·9068 at 15° ; soluble in about 11 parts of water ; miscible in all proportions with alcohol, ether, and acetic acid.

Reaction.—Weigh out 20 grams of ethyl acetate, and heat in a round flask with three times its volume of aqueous potash ($1KOH : 3H_2O$) with upright condenser over wire-gauze. Add a small piece of porous pot to prevent bumping. After an hour or so the upper layer of ethyl acetate will have disappeared. Distil the product with a thermometer until the temperature reaches 100°. Add solid potassium carbonate to the distillate until no more dissolves. Separate the top layer of alcohol and dehydrate over fresh potassium carbonate or quicklime. Distil with a thermometer and weigh the distillate. Neutralise the alkaline liquid, from which the alcohol was distilled, with dilute sulphuric acid, and evaporate to dryness on the water-bath. Break up the solid residue, and distil with concentrated sulphuric acid (20 c.c.), until the thermometer marks 130°. Redistil and collect

between 115° and 120°. Weigh the distillate. This process furnishes an example of *hydrolysis* or *saponification*,

$$CH_3.COOC_2H_5 + H_2O = CH_3.COOH + C_2H_5OH$$
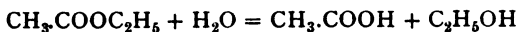
PREPARATION 16.

Ethyl Acetoacetate (Acetoacetic Ester),
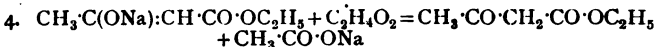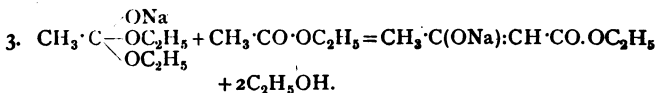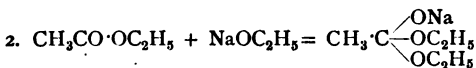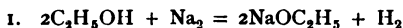$$CH_3.CO.CH_2.CO.OC_2H_5.$$

Geuther (1863), *Jahresb.*, 323 : Frankland, Duppa (1865), *Phil Trans.*, 156, 37 ; Wislicenus (1877), *Ann.*, 186, 161

200 grms. ethyl acetate.
20   „   sodium.

The ethyl acetate, carefully dehydrated as described in the previous preparation, is introduced into a round flask (½ litre) connected with a long upright condenser. 20 grams well pressed sodium, cut into thin slices, are quickly added, and the flask cooled in water. After a short time a brisk reaction sets in, and ultimately the liquid boils. When the first action is over, and no further evolution of heat occurs, the mixture is heated on the water-bath, without detaching the condenser, until the sodium is completely dissolved. A 50 per cent. acetic acid solution is at once added and well shaken, until the liquid is acid (about 100 c.c.), and then an equal volume of concentrated brine. The liquid divides into two layers ; the upper one, consisting of acetoacetic ester and unchanged ethyl acetate, is carefully separated. It is distilled over wire-gauze until the thermometer marks 100°, and all the ethyl acetate has been removed. The distillate is now collected in five fractions (100—130°, 130—135°, 165—175°, 175—185°, 185—200°). The fraction distilling at 175—185° is nearly pure acetoacetic ester. Yield 30—40 grams. A further quantity may be obtained by redistilling the other fractions ; but it is undesirable to repeat the process frequently, as acetoacetic ester gradually decomposes at the boiling point. It is for this reason that Gattermann recommends the fractional distillation to be carried out *in vacuo*.

The brown residue remaining in the distilling flask solidifies, on cooling, to a crystalline mass consisting chiefly of dehy-

dracetic acid $C_8H_8O_4$. It is converted into the sodium salt by boiling with soda solution with the addition of animal charcoal. The sodium salt crystallises from the filtrate. On adding dilute sulphuric acid, the free acid is obtained as colourless needles ; m. p. $109°$.

1. $2C_2H_5OH + Na_2 = 2NaOC_2H_5 + H_2$

2. $CH_3CO \cdot OC_2H_5 + NaOC_2H_5 = CH_3 \cdot C \overset{\diagup ONa}{\underset{\diagdown OC_2H_5}{-OC_2H_5}}$

3. $CH_3 \cdot C \overset{\cdot ONa}{\underset{\diagdown OC_2H_5}{-OC_2H_5}} + CH_3 \cdot CO \cdot OC_2H_5 = CH_3 \cdot C(ONa){:}CH \cdot CO \cdot OC_2H_5$
$+ 2C_2H_5OH.$

4. $CH_3 \cdot C(ONa){:}CH \cdot CO \cdot OC_2H_5 + C_2H_4O_2 = CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot OC_2H_5$
$+ CH_3 \cdot CO \cdot ONa$

The formation of ethyl acetoacetate occurs, according to Claisen, in four steps. The presence of a small quantity of alcohol gives rise to sodium ethylate, which forms an additive compound with ethyl acetate. The latter unites with a second molecule of ethyl acetate yielding the sodium salt of ethyl acetoacetate, and splitting off alcohol, which reacts with fresh metallic sodium. The sodium salt on acidifying passes into the tautomeric (ketonic) form of acetoacetic ester.

Properties.—Colourless liquid possessing a fruity smell ; b. p. $182°$; sp. gr. $1·03$ at $15°$. Boiled with dilute caustic potash, the ester decomposes into alcohol, carbon dioxide, and acetone (ketonic decomposition), with strong or alcoholic caustic potash, sodium acetate and alcohol are formed (acid decomposition).

Reactions.—1. Add a drop of ferric chloride to a few drops of the ester ; a deep violet coloration is produced.

2. Add 1 c.c. of a saturated alcoholic solution of cupric acetate to a few drops of the ester, a bluish green crystalline precipitate of copper acetoacetic ester $(C_6H_9O_3)_2 Cu$, is formed.

Distillation in vacuo.—The apparatus is shown in Fig. 51. The distilling flask is provided with a thermometer and attached ▉▉▉▉▉▉▉▉▉▉▉▉▉ receiver. The receiver consists of a

second distilling flask, which is tightly attached to the end of the condenser and connected by the side limb by means of pump-tubing to a water-jet aspirator and mercury-gauge. Some
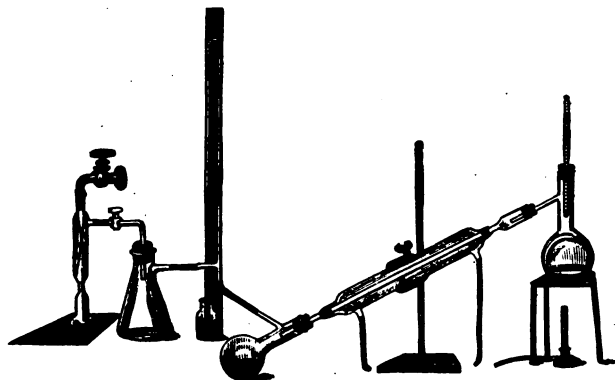
FIG. 51.

small bits of porous pot are placed in the flask and the apparatus exhausted to about 35—40 mm. pressure. At this pressure ethyl acetoacetate boils at about 90°. The following table gives the temperatures corresponding to different pressures :—

t.	mm.	t.	mm.
74°	14	94°	45
79°	18	97°	59
88°	29	100°	80

The chief inconvenience which attends distillation *in vacuo* is the bumping of the liquid in the distilling flask. This may be moderated or removed by various devices, such as the introduction of porous pot, capillary glass tubes, &c., or by driving a rapid stream of fine air-bubbles through the liquid. For this purpose a Claisen flask (Fig. 52), may be used with advantage. A tube is drawn out into a fine capillary and is open at both ends, the wide end being attached to a short piece of rubber tubing and screw-clip. This tube is inserted through a cork in

the straight neck of the flask, whilst the thermometer is fixed in
the second neck, which is attached to the condenser. The stream
of air-bubbles is regulated by the clip.
Instead of the long manometer shown
in Fig. 51, a more compact, and, for low
pressures, a more convenient form is
shown in Fig. 53. If the distillate has
to be separated into fractions it is unde-
sirable to interrupt the boiling. Various
forms of apparatus for
effecting this object are
shown in Figs. 54—56. The
apparatus (Fig. 54) consists
of a double receiver a and
b; c and e are ordinary two-
way taps, whilst d is a
three-way tap pierced
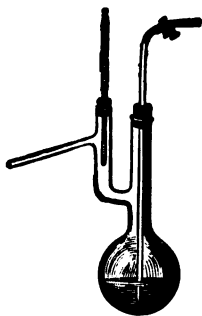
FIG. 52.

FIG. 53.

lengthwise and crosswise as shown in section
at f. The aspirator is attached to the limb marked with the arrow.
During the distillation the taps c and d connect the apparatus with

FIG. 55.

FIG. 54.

FIG. 56.

the aspirator whilst e is closed. The distillate collects in a. When
this fraction is to be removed c is closed and e is opened. The

liquid is thereby transferred to the second receiver b ; e is now closed, c is opened and d turned so as to let air into b ; b may now be removed and replaced by a similar vessel and the process repeated. Fig. 55 needs little 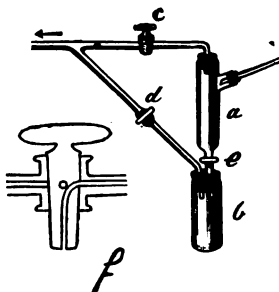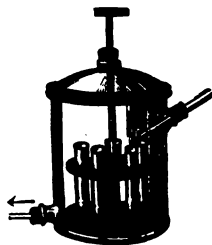explanation. There are two or more receivers on one stem. By rotating the stem the distillate falls into one or other receiver. Fig. 56 consists of a vacuum vessel containing a series of test-tubes which can be moved in turn, under the end of the condenser, by means of a vertical axis. It is often preferable to heat the distilling flask in an oil or metal bath instead of using wire-gauze. Distilling flasks above 250 c.c. capacity should not be used for low pressures, as they may collapse. For high boiling liquids, or for substances which may solidify in the condenser, a condenser tube without water-jacket is used, and in certain cases it is found convenient to slip the side-tube of the distilling flask directly into the neck of the receiver.

PREPARATION 17.

Monochloracetic Acid, $CH_2Cl.CO.OH$.

R. Hofmann (1857), *Ann.*, 102, 1 ; Auger, Béhal (1889), *Bull. Soc. Chim.* (3) 2, 145.

100 grms. glacial acetic acid.
10 „ sulphur (flowers).

Fit up the apparatus shown in Fig. 57.* It consists of a stoneware jar one-third full of pyrolusite in lumps, and fitted with exit tube and tap-funnel. It is heated on a sand-bath over a small flame, whilst concentrated hydrochloric acid is allowed to drop in from the tap-funnel. A rapid current of chlorine is thus evolved, which is dried by passing through concentrated sulphuric acid in the Woulff bottle. The Woulff bottle has a safety and exit tube, the latter being connected with a straight tube passing to the bottom of the retort. The retort is tilted upwards and connected with an upright condenser, which is furnished with an open calcium chloride tube. The acetic acid and sulphur are placed in the retort, and heated on the water-bath. The retort and contents are weighed at the commencement of the operation on a rough balance. A rapid current of chlorine

is then passed through for six to twelve hours, and the retort
occasionally weighed, until the increase in weight (50 grams)
roughly corresponds to the formation of monochloracetic acid.
The operation is then stopped.   The action of the chlorine is
greatly facilitated by sunlight.   The yellow liquid in the retort
is decanted from the sulphur into a distilling flask, and distilled
over wire-gauze.   Some acetyl chloride, sulphur chloride, and
unchanged acetic acid first distil, after which the temperature

FIG. 57.

rises and the fraction boiling at 150°—190° is collected separately.
It is advisable to run the water out of the condenser when the
temperature approaches 170°, as the acid may solidify and block
the condenser-tube.   The distillate solidifies on cooling.   Any
liquid is drained off at once, and the solid is redistilled and col-
lected at 180°—190°.   It is nearly pure chloracetic acid.   Yield
80—100 grams.

$$CH_3.CO.OH + Cl_2 = CH_2Cl.CO.OH + HCl.$$
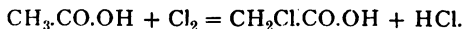
The sulphur acts as a "chlorine carrier" by forming sulphur
chloride.

Properties.—Colourless crystals ; m. p. 63° ; b. p. 185°—187° ;
readily soluble in water, and deliquescent in moist air.   It causes
blisters on the skin.

PREPARATION 18.

Monobromacetic Acid, $CH_2Br.COOH$.

Hell (1881), *Ber.*, 14, 891 ; Volhard (1887), *Ann.*, 242, 141 ; Zelinsky (1887), *Ber.*, 20, 2026.

> 30 grms. (30 c.c.) glacial acetic acid.
> 105 „ (35 c.c.) bromine.
> 5 „ red phosphorus.

All the above substances must be dry. The acetic acid is frozen in ice, and any liquid drained off, and the red phosphorus is washed with water to free it from phosphoric acid, dried in the steam oven, and kept over sulphuric acid in a desiccator until required. The bromine is placed in a separating funnel with half its volume of concentrated sulphuric acid overnight, and then separated. The apparatus is shown in Fig. 58. It consists of a round flask (250 c.c.) attached to an upright condenser, which is provided with a cork. A tap-funnel containing the bromine passes through one hole, and a wide bent tube, attached at its lower end to a funnel, passes through the other. As a large quantity of hydrobromic acid is evolved in the reaction, the funnel is made to touch the surface of water contained in a beaker, whereby it is completely absorbed. The phosphorus and acetic acid are placed in the flask, and bromine dropped in from the tap-funnel.* A vigorous reaction occurs, and the liquid becomes very warm. After half the bromine has been added the action moderates, and the remainder may be added more quickly. When the whole has been

FIG. 58.

added, the liquid is boiled gently until the colour of the bromine disappears. It is now allowed to cool, and the liquid decanted into a distilling flask for distillation *in vacuo*. Care must be taken not to touch the substance with the hands, as even a small quantity produces very unpleasant sores. The apparatus for distilling *in vacuo* is shown in Fig. 51 (p. 77).
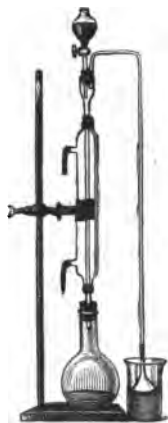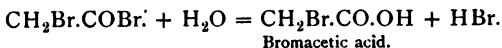
The distilling flask is provided with a thermometer, and attached to a short condenser and receiver. The receiver consists of a second distilling flask, which is tightly attached to the end of the condenser and connected by the side limb with pump-tubing to a water-jet aspirator and mercury manometer. Some small bits of of porous pot are placed in the flask, and the apparatus exhausted to about 50—60 mm. pressure. The liquid distils at a nearly constant temperature (about 50°—53°), and consists of nearly pure bromacetylbromide. The calculated quantity of water is added to convert it into bromacetic acid, when the liquid forms a solid crystalline mass. It may be purified by distillation at atmospheric pressure with condenser-tube only, the portion boiling above 165° being collected separately.

$$3CH_3.CO.OH + P + 4Br_2 = 3CH_2Br.COBr. + HPO_3 + 2HBr.$$

<div align="center">Bromacetyl bromide.</div>

$$CH_2Br.COBr. + H_2O = CH_2Br.CO.OH + HBr.$$

<div align="center">Bromacetic acid.</div>

Properties.—Colourless crystals ; m. p. 50°—51° ; b. p. 208°.

PREPARATION 19.

Glycocoll (Glycine, Amidoacetic Acid). $CH_2 {<}^{NH_2}_{CO.OH}$.

Braconnot (1820), *Ann. Ch. Phys.* (2) 13, 114 ; Perkin, Duppa (1859), *Chem. Soc. J.*, 11, 22 ; Kraut (1891), *Ann.*, 266, 292.

> 50 grms. chloracetic acid.
> 50 c.c. water.
> 600 c.c. ammonia, 26·5 per cent. (sp. gr. ·907 at 14°).

Fit up the apparatus shown in Fig. 59. It consists of a large wide-necked bottle, in which the ammonia solution is placed. The solution is stirred by a mechanical stirrer, rotated by means of a water-turbine. The solution of the chloracetic acid in 50 c.c. water, is dropped in from a tap-funnel. After standing 24 hours the liquid is poured into a flask, and the excess of ammonia is removed by passing in a current of steam, and then evaporating on the water-bath until the last traces of ammonia disappear. The solution now contains glycocoll and ammonium

chloride. Precipitated carbonate of copper is added to the hot liquid until no further effervescence occurs, and some carbonate remains undissolved. It is filtered and evaporated down on the water-bath until crystallisation sets in. This is determined by removing and cooling a small portion in a test tube or watch-glass. The blue needles of copper glycocoll, $(C_2H_4NO_2)_2Cu.H_2O$, are filtered and washed, first with dilute and then with stronger methylated spirit. The mother liquor may be further evaporated, and a fresh quantity of crystals obtained. The copper salt is dissolved in water and precipitated hot with sulphuretted hydrogen, the free glycocoll passing into solution. The precipitate is filtered and well washed, and the filtrate evaporated

FIG. 59.

to a small bulk on the water-bath. Crystals of glycocoll separate out. Yield 15-20 grams. The loss is due to the formation of di- and triglycolaminic acid, $NH(CH_2.COOH)_2$ and $N(CH_2COOH)_3$.

$$CH_2Cl.COOH + 2NH_3 = CH_2NH_2.COOH + NH_4Cl.$$
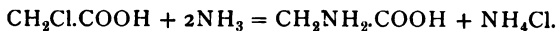
*Properties.*—Large monoclinic crystals ; discoloured at 228° ; m.p. 232-236' ; scarcely soluble in alcohol and ether, readily soluble in water (1 part glycocoll in 4 parts water).

Reaction.—1. Add a drop of copper sulphate to a solution of glycocoll, and notice the blue colour of the copper salt.

2. Add a drop of ferric chloride to the solution. It gives a deep red colour.

G 2

<center>PREPARATION 20.</center>

Diethyl Malonate. $CH_2\begin{cases} CO.OC_2H_5 \\ CO.OC_2H_5 \end{cases}$
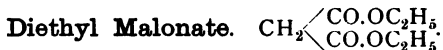
Conrad (1880) *Ann.*, 204,126 ; Claisen, Crismer (1883) *Ann.*, 218, 131.

<center>
50 grms. monochloracetic acid.
100   ,,   water.
38   ,,   potassium carbonate.
38   ,,   potassium cyanide (pure).
</center>

The monochloracetic acid is dissolved in 100 c.c. water in a porcelain basin, and the solution neutralised with 38 grams potassium carbonate.* Thirty-eight grams powdered potassium cyanide are now added, and the mixture heated on the sand-bath until the reaction sets in with strong ebullition. When the reaction is over, the contents of the basin are evaporated as rapidly as possible on the sand-bath, with constant stirring, until a thermometer inserted into the brown semi-fluid mass indicates a temperature of 135°. The mass is allowed to cool without interrupting the stirring, and, when cold, the hard saline deposit, consisting of potassium chloride and potassium cyan-acetate, is finely powdered, weighed, and introduced into a round flask connected with an upright condenser. Two-thirds the weight of absolute alcohol is added, and the mixture, heated on the water-bath, is saturated with dry hydrochloric acid gas.*

Preparation of Dry Hydrochloric Acid Gas.—A filter flask ($\frac{1}{2}$ litre) is fitted with a rubber cork, through which a tap-funnel is inserted. The flask is filled one-third full of comm. conc. hydrochloric acid, and is attached to a wash-bottle containing a little conc. sulphuric acid. A delivery-tube is attached to the wash-bottle. The hydrochloric acid gas is generated by dropping into the flask containing the acid, conc. sulphuric acid from the tap-funnel. The acid must be run in rather more quickly at the commencement than is requisite later on. The apparatus is shown in Fig. 60.

The gas is conducted in through a wide adapter to prevent the inlet-tube becoming choked with the crystalline precipitate

which is formed. Even this is not always effective, and the tube should be occasionally cleared by detaching the connection and pushing down a long glass rod. When hydrochloric acid has been passed in for about ten hours, the contents of the flask are cooled, poured into ice-water, and shaken with 150 c.c. commercial ether, in which the ethyl malonate dissolves. The ethereal layer is then separated from the acid liquid, shaken

FIG. 60.

with a little dilute potassium carbonate solution, drawn off, dehydrated over calcium chloride, and distilled on the water-bath. When the ether has been driven off, the greater portion of the residue distils at 190—200°. Yield about 40 grams.

$$CH_2Cl.CO_2K + KCN = CH_2.CN.CO.OK + KCl.$$
$$CH_2CN.CO.OH + 2C_2H_5OH + HCl = CH_2(CO_2C_2H_5)_2 + NH_4Cl.$$
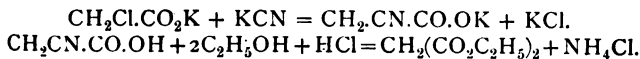
Properties.—Colourless liquid; b.p. 195°; sp. gr. 1.068 at 18°; insoluble in water.

PREPARATION 21.

Ethyl Malonic Acid. $C_2H_5.CH\begin{cases}CO_2H\\CO_2H\end{cases}$

Conrad (1880), *Ann.*, 204, 134.

$$
\begin{array}{rll}
16 & \text{grms.} & \text{ethyl malonate} \\
25 & \text{,,} & \text{absolute alcohol} \\
2\cdot3 & \text{,,} & \text{sodium} \\
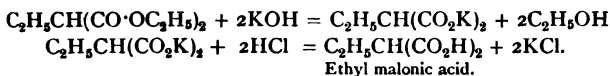20 & \text{,,} & \text{ethyl iodide}
\end{array}
$$

Sodium ethylate is first prepared by dissolving 2·3 grms. sodium in 25 grms. alcohol, and the reaction completed, if necessary, on the water-bath as described on p. 75. Whilst the product is still slightly warm, 16 grms. malonic ester are added from a tap-funnel. The liquid remains clear at first, but before the ester has all been added a white crystalline body (sodium ethyl malonate) separates out, and soon the whole solidifies. To the solid mass 20 grms. ethyl iodide are slowly added. The mass softens and, after continued shaking, completely liquefies with evolution of heat. The product is now heated on the water-bath when it becomes turbid from the separation of sodium iodide in the form of a fine powder. After one and a half hours the liquid ceases to be alkaline and the reaction is complete. The alcohol is distilled off from a brine-bath (water saturated with common salt). On the addition of water to the residue an almost colourless oil separates out. The oil is separated by extraction with ether, dehydrated over calcium chloride and distilled. When the ether has been driven off, almost the whole of the residue (ethyl diethyl malonate) passes over at 206 – 208°. Yield about 15 grams.

$$CH_2(CO.OC_2H_5)_2 + NaOC_2H_5 = CHNa(CO.OC_2H_5)_2 + C_2H_5OH$$
<div align="center">Sodium ethyl malonate.</div>

$$CHNa(CO.OC_2H_5)_2 + C_2H_5I = CH(C_2H_5)(CO.OC_2H_5)_2 + NaI$$
<div align="center">Ethyl malonic ester.</div>
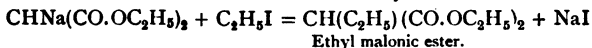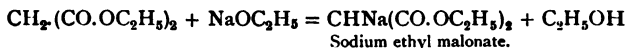
*Properties.*—Colourless liquid with an agreeable fruity smell ; b. p. 207°, sp. gr. 1·008 at 18°.

To obtain the free acid, the ester is hydrolysed with caustic potash. To 15 grams caustic potash in strong

aqueous solution, 10 grams of the ester are slowly added from a tap-funnel. At first an emulsion forms, which soon solidifies to a white mass. This is heated on the water-bath with constant shaking for about three-quarters of an hour, until it becomes completely liquid. The hydrolysis is then complete. The product is diluted with a little water, neutralised with concentrated hydrochloric acid, and the free acid precipitated with a strong solution of calcium chloride as the calcium salt. This is separated from the solution by filtration and concentrated hydrochloric acid added to the calcium salt. From the acid solution the free ethyl malonic acid is extracted by shaking with ether. After evaporating off the ether, the acid remains behind as a syrup, which solidifies when cold. This is redissolved in water, boiled with a little animal charcoal to free it from any adhering colouring matter, filtered, and evaporated to syrupy consistency on the water-bath. The colourless acid crystallises on cooling. Yield about 5 grams.

$$C_2H_5CH(CO \cdot OC_2H_5)_2 + 2KOH = C_2H_5CH(CO_2K)_2 + 2C_2H_5OH$$
$$C_2H_5CH(CO_2K)_2 + 2HCl = C_2H_5CH(CO_2H)_2 + 2KCl.$$
$$\text{Ethyl malonic acid.}$$

Properties.—Rhombic prisms ; m.p. 111·5°, easily soluble in water, alcohol, and ether.

Reaction.—1. Heat a gram or two of the acid in a test-tube over a small flame and have at hand a second test-tube one-third full of lime water The acid decomposes at 160° into butyric acid and carbon dioxide. When the effervescence begins to slacken, decant the gas downwards into the test-tube of lime-water, shake up and notice the turbidity. The acid which remains will have a strong smell of butyric acid.

$$C_2H_5CH(CO_2H)_2 = C_3H_7CO.OH + CO_2$$

Chloral Hydrate, $CCl_3.CH{<}^{OH}_{OH}.$
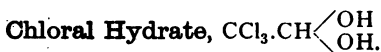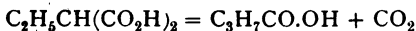
Liebig (1832), *Ann.* 1, 189 ; Dumas (1834) *Ann. Chim. Phys.*, 56, 123.

Chloral hydrate is obtained by the action of chlorine upon ethyl alcohol. The solid chloral alcoholate is formed,

$CCl_3.CHOH.OC_2H_5$, which, when decomposed with sulphuric acid, yields chloral $CCl_3.COH$, a liquid which combines with water to form the crystalline hydrate.

Properties.—It crystallises in prisms, which dissolve easily in water, alcohol, and liquid hydrocarbons. It has a peculiar smell ; m. p. 50—51° ; b. p. 97·5°. It volatilises on evaporating its aqueous solution.

Reactions.—1. Add a few drops of a solution of chloral hydrate to a litt[le ammonio-silver nitrate solution and warm. Metallic silver will be deposited.

2. Add a little caustic soda to a solution of chloral and warm gently. The heat of the hand is sufficient for the purpose. A smell of chloroform is at once apparent, $CCl_3.CH(OH)_2 + NaOH = CHCl_3 + HCO.ONa + H_2O$. Sodium formate remains in solution.

3. Add a few drops of ammonium sulphide solution and warm gently. A brown colouration or precipitate is formed.

<div align="center">PREPARATION 22.</div>

<div align="center">

Trichloracetic Acid, $CCl_3.CO.OH$

</div>

Dumas (1838), *Compt. rend.*, 8, 609 ; Clermont (1871), *Ann. Chim. Phys.* (6), 6, 135.

> 25 grms. chloral hydrate
> 20   „   fuming nitric acid ; sp. gr. 1·5 (see p. 20).

The chloral hydrate is melted in a flask (250 c.c.) and the fuming nitric acid added.* The mixture is heated carefully over a small flame until the reaction sets in. After a few minutes red fumes are evolved, consisting mainly of nitrogen tetroxide. The reaction proceeds without the application of heat, and is complete when, on warming the liquid, nitrous fumes cease to come off. The product is now distilled ; below 123° excess of nitric acid distils ; between 123° and 194° a mixture of trichloracetic acid and a small quantity of nitric acid pass over, and at 194—196° nearly pure trichloracetic acid collects in the receiver and solidifies on cooling. It is advisable to distil the last fraction with a condenser-tube only. The

fraction boiling at 123—190° is treated with a fresh quantity of fuming nitric acid (10 c.c.), and the product purified as before. Yield, 10—15 grams.

$$CCl_3.CO.H + O = CCl_3.CO.OH.$$
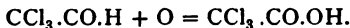
Properties.—Colourless, rhombohedral crystals; m.p. 55°; b.p. 195°.

PREPARATION 23.

Oxalic Acid, $\begin{array}{c} CO.OH \\ | \\ CO.OH \end{array} + 2H_2O$
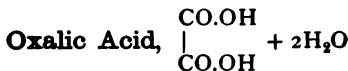
Scheele (1776).

250 grms. conc. nitric acid.
50 „   cane sugar.

The nitric acid is warmed on the water-bath in a large flask (1½ litre) to the temperature of boiling water. It is then placed in the fume cupboard and the cane sugar at once added. Torrents of brown fumes are evolved, and when the reaction has ceased, the liquid is evaporated on the water-bath to one-quarter its bulk.* On cooling, large colourless crystals of the acid separate. They are drained on a small porcelain-funnel without filter paper, and recrystallised from a very small quantity of water. Yield, 10-15 grams.

Properties.—Colourless crystals, which, on heating to 100°, lose their water of crystallization, melt, and then partly sublime and partly decompose, giving off carbon dioxide and formic acid. M.p. of the hydrated crystals 101·5°. Soluble in water, and in alcohol, very slightly soluble in ether.

Reactions.—1. Boil a little of the acid with ammonia solution until neutral, and add calcium chloride solution. A white precipitate of the calcium salt is obtained, which is insoluble in acetic acid.

2. Add to a solution of the acid a few drops of dilute sulphuric acid, and warm gently. On adding permanganate solution it is immediately decolourised, $5C_2H_2O_4 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + 8H_2O + K_2SO_4 + 2MnSO_4.$

3. Heat two or three grams of the crystals with about 5 c.c. concentrated sulphuric acid.   Rapid effervescence occurs, and the gas may be ignited at the mouth of the tube, $C_2H_2O_4 - H_2O = CO + CO_2$.

PREPARATION 24.

Methyl Oxalate.

Dumas, Peligot (1836) *Ann. Chim. Phys.*, 58, 44 ; Erlenmeyer, *Rep. Pharm.* (2) 23, 432.

> 70 grms. crystallised oxalic acid
> 50   „   methyl alcohol.

The oxalic acid is powdered and heated in a basin on a waterbath, which is kept boiling briskly, until no more water is given off

(one to two hours). It must be occasionally stirred and powdered up.   It is then heated to 110—120° in an air-bath or in a Victor Meyer drying apparatus (see Fig. 61) until it loses the weight corresponding to two molecules of water. This drying apparatus consists of a jacketed copper vessel fixed upon a tripod.   A liquid of constant boiling point is poured into the outer jacket, and the vapours are condensed by an upright condenser which is attached to the outlet tube. The substance is placed within and covered with a metal lid. There is a small aperture to admit air from below into the inner vessel, and a corresponding outlet in the lid.   Amyl alcohol, b. p. 132°, may be used in the outer jacket in the present case.

The dehydrated and powdered oxalic acid is mixed with the methyl alcohol, and the mixture heated on the water-bath for two hours with an upright con-

FIG. 61.

denser. The liquid is then distilled with a thermometer. When the temperature rises to 100° the receiver is replaced by a

beaker, and the water-jacket of the condenser removed. The thermometer rises rapidly to the boiling point of methyl oxalate 160—165°, and the distillate solidifies in the receiver. It is drained at the pump and dried. It may be recrystallised from methylated spirit. Yield, 20-25 grams.

$$C_2H_2O_4 + 2CH_3OH = C_2O_2(OCH_3)_2 + 2H_2O.$$
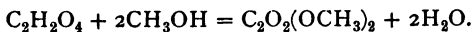
Properties.—Colourless plates ; m. p. 54° ; b. p. 163°.

Reactions.—For this purpose the alcoholic mother liquor from the crystals may be used.

1. Add a little caustic potash solution. Crystals of potassium oxalate are deposited. The ester is hydrolysed.

2. Add a few drops of concentrated ammonia. A white crystalline precipitate of oxamide is formed, $C_2O_2(OCH_3)_2 + 2NH_3 = C_2O_2(NH_2)_2 + 2CH_3OH.$

PREPARATION 25.

Palmitic Acid. $C_{15}H_{31}CO.OH.$

Fremy (1840), *Ann.*, 36, 44.

30 grms. palm oil
24   „   caustic potash.

The caustic potash is dissolved in its own weight of water. The palm oil is melted in a large basin on the water-bath, and the potash solution added with constant stirring. The mixture is heated for half an hour. Half a litre of boiling water is poured in, and, after stirring well, 75 c.c. concentrated hydrochloric acid are gradually added, and the heating continued until the palmitic acid separates out as a transparent brown oil on the surface of the liquid. It is allowed to cool, and the cake of impure acid removed and pressed between filter-paper. The acid is now melted in a small basin on the water-bath and decanted, from any water which may have separated, into a retort (250 c.c.). It must be distilled *in vacuo.* The neck of the retort is fixed into a small filtering tube, which serves as receiver, as shown in Fig. 62. A few small pieces of unglazed pot are dropped into the retort, the tubulus of which is closed with a cork holding a thermometer. Before commencing the

distillation the apparatus should be tested to see that it is air-tight. It is then evacuated with the water pump (see Fig. 31 p. 39), and the distillation commenced. During the distillation it is advis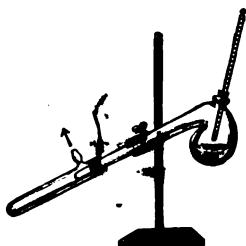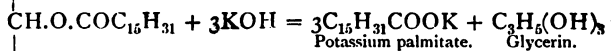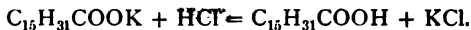able to hold the Bunsen and to heat the retort with the bare flame. Under a pressure of 36 mm. the acid distils at 245°. The pale yellow oil which collects in the receiver, is poured out into a basin whilst hot and allowed to cool. The cake of acid is spread on a porous plate and left to drain, when it becomes nearly colourless, and, after one or two crystallizations from small quantities of methylated spirit, is pure, and melts at 62°. Yield about 20 grams. The aqueous portion from which the cake of acid is removed contains free hydrochloric acid, potassium chloride, and glycerin. The latter may be obtained by evaporating to dryness on the water-bath, and extracting the residue with small quantities of alcohol, which dissolves out the glycerin. On evaporating the alcohol impure glycerin is left.

FIG. 62.

$$CH_2.O.CO.C_{15}H_{31}$$
$$CH.O.COC_{15}H_{31} + 3KOH = 3C_{15}H_{31}COOK + C_3H_5(OH)_3$$
$$CH_2.O.CO.C_{15}H_{31}$$

Palmitin.   Potassium palmitate.   Glycerin.

$$C_{15}H_{31}COOK + HCl = C_{15}H_{31}COOH + KCl.$$

Properties.—Crystallises in tufts of colourless needles ; m.p. 62° ; soluble in alcohol and ether ; insoluble in water.

Reactions.—1. Dissolve a small quantity of the acid in caustic soda solution and add salt. Sodium palmitate separates as a curdy white precipitate.

2. Boil another portion of the acid with caustic soda and let it cool. Pour off the liquid from the crust of sodium palmitate, which forms on the surface, wash once or twice with a little cold water, and dissolve the sodium salt in hot water. On cooling, a thick gelatinous mass of sodium palmitate separates.

Glycerin (C██████████$_2$(OH).CH(OH).CH$_2$(OH).

████████), *Opusc.*, 2, 175.

Glycerin is ████████ the hydrolysis of fats and oils, and purified by dist████████ under reduced pressure with superheated steam.

Properties.—A viscid colourless liquid, with a sweet taste b.p 290°. It boils, *under ordinary pressure*, with partial decomposition forming acrolein; sp. gr. 1·269 at 12°, ████████ le with water and alcohol; insoluble in ether and the h██████████s.

Reactions.—1. Heat a few drops of gl██████████ some powdered potassium hydrogen sulphate. The █████████ smell of acrolein is at once perceptible.

2. Make a borax bead and dip it into a solution of glycerin and bring it into the flame. A green colouration due to boric acid is produced.

PREPARATION ████

Formic Acid. ████

Berthelot (1856), *Ann. Chim. Phys.* (3), 46, 477; Lovi██ (1866) *Bull. Soc. Chim.* (2) 5, 7; (1870), (2) 14, 367.

██50 grms. anhydrous glycerin.
██200 „ oxalic acid (in four p██████ d .50 grams).

The glycerin is dehydrated by h██████ng it gently in a basin on a sand-bath until a thermometer w██h the bulb immersed in the liquid indicates 175°. Fifty gra██ of commercial crystallised oxalic acid and fifty grams of glycerin are heated in a retort (250 c.c.) over wire-gauze, with condenser and receiver. A thermometer is fixed through the tubulus with the bulb in the liquid. The reaction begins at about 80°, and at 90° proceeds briskly, carbon dioxide being evolved. The temperature is maintained at 105—110° until the evolution of gas has slackened. Some aqueous ████ acid has meanwhile collected in the receiver. The c██████ of the retort are now cooled to about 80°, and a further 50 grams of oxalic acid added. The reaction recommences on heating with the formation of aqueous formic acid, which becomes more concentrated with each fre██

addition of oxalic acid until the ▓▓▓▓ ▓▓entually contains 56 per cent. of acid. The other ▓ortions of ▓▓ic acid are added in the same way. In order to ▓▓ain the ▓rmic acid which remains as monoformin in the retort, the contents are transferred to a round flask, diluted with about 250 c.c. of water and distilled in steam, until the distillate has only a faintly acid reaction (about 250 c.c.). The apparatus for distilling in steam is shown in Fig. 63. A large flask, or, preferably, a 1 gallon
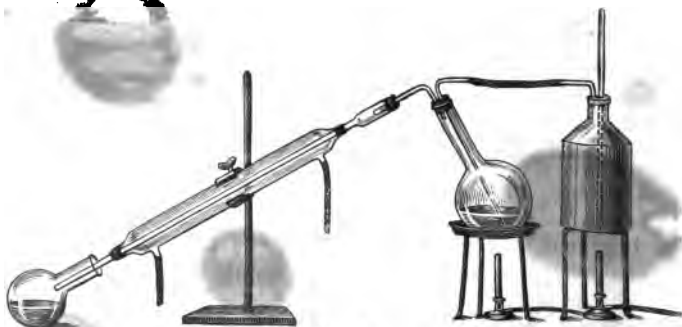

FIG. 63.

tin is closed by a double bored cork. A safety-tub▓ ▓▓ses through one hole, ▓▓▓ a bent tube which terminates be▓▓ the cork passes through th▓ ▓cond hole, and is attached by rubber tubing to the inlet-tube of the distilling flask (1 litre). The flask is sloped to prevent the contents being splashed over into the condenser. It is heated on the sand-bath or asbestos board to boiling, and steam passed in. The united distillates are poured into a basin and neutralised by adding lead carbonate until, on heating, no further effervescence occurs. The liquid is now left for a moment to settle, and the clear solution decanted, whilst hot, through a fluted filter. The residue in the basin is boiled up again with a volume of water equal to that decanted, and again a third and fourth time, and filtered hot each time. The lead formate will have now passed into solution and the liquid is then evaporated down on a sand-bath or ring-burner (see Fig. 64), until crystals appear on the surface, when the liquid is put on one side to cool. Lead formate crystallises out

in long white needles. Yield about 50 grams. In order to obtain pure formic acid, sulphuretted hydrogen is passed over the heated lead salt. As a rule, however, the quantity is too small to make this operation worth while. It is carried out as follows :

The powdered salt, dried on the water-bath, is introduced in a long layer into a sloping wide tube, loosely stopped at the lower end by a plug of glass wool or asbestos.* To the lower end of the tube a receiver, in form of a distilling-flask, is attached, which is protected from moisture by a drying-tube. The salt is heated gently by moving a flame along the tube whilst sulphuretted hydrogen, washed through water, and dried by passing through a U-tube containing calcium chloride, is led over the salt in not too rapid a stream. The lead formate blackens, and is slowly converted into lead sulphide and formic acid, which drops into the receiver. The acid, which retains a strong smell of sulphuretted hydrogen, is freed from the latter by distillation over a little dry lead formate. Yield 10 grams.

FIG. 64.

$$C_3H_5(OH)_3 + C_2H_2O_4 = C_3H_5{}^{(OH)_2}_{O.COH} + CO_2 + H_2O.$$

Glycerin monoformin.

$$C_3H_5{}^{(OH)_2}_{O.COH} + H_2O = HCO.OH + C_3H_5(OH)_3.$$

Formic acid.
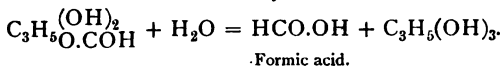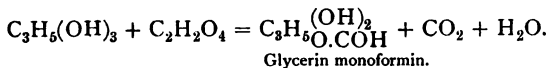
Properties.—Colourless liquid, with a penetrating smell resembling sulphurous acid ; b. p. 99° ; sp. gr. 1·223 at 0° ; solidifies below 0° to colourless crystals ; m.p. 8·6° ; soluble in water and alcohol.

Reactions.—For the following tests use a solution made as follows :—Boil a little lead formate with a solution of sodium carbonate, filter, add a slight excess of nitric acid, boil a minute, add dilute ammonia and boil until neutral. 1. Add a drop of ferric chloride. A red colouration is produced, which, on boiling, becomes turbid from the formation of basic ferric formate. (Compare acetic acid, p. 67.)

2. Add to the solution a few drops of a solution of silver nitrate and warm. Metallic silver is deposited as a black powder.

3. Add to the solution a few drops of a solution of mercuric chloride and warm. White mercurous chloride is deposited.

4. Add concentrated sulphuric acid to a little solid lead formate and heat. Carbon monoxide is evolved, and may be lighted at the mouth of the test-tube. $(HCOO)_2Pb + H_2SO_4 = PbSO_4 + 2H_2O + 2CO.$

RREPARATION 27.

Allyl Alcohol. $CH_2 : CH.CH_2OH.$

Tollens, Henninger (1870), *Ann.*, 156, 129

50 grms. oxalic acid.
200   ,,   glycerin.
¼   ,,   ammonium chloride.

A mixture of the above substances are heated in a retort (½ litre) over wire-gauze with condenser and receiver.* A rapid evolution of carbon dioxide at first occurs, and the temperature, indicated by a thermometer dipping into the liquid, remains for some time stationary at about 130°. As the temperature slowly rises the evolution of gas slackens, and after a time (at about 180°) entirely ceases. When the temperature has reached 195° the receiver, which contains aqueous formic acid, is changed. At 200—210° carbon dioxide is again given off, and oily streaks are observed to run down the neck of the retort ; at the same time a disagreeable penetrating smell is perceptible. By gently heating the contents of the retort, a temperature of 220—230° is maintained for some time, and when it has finally risen to 260° the distillation is stopped. The distillate is a mixture of allyl alcohol and water, and there is also present allyl formate, glycerin, and acrolein. Excess of glycerin remains in the retort and may be used again by repeating the operation with a smaller quantity of oxalic acid (30—40 grams) until the residue is too small or has become dark-coloured and thick. The distillate is submitted to a second distillation, which is continued until no oily layer separates from the latter portions which distil on treating with solid potassium carbonate. This occurs when the temperature reaches about 105°. On adding solid potassium carbonate to the distillate, the allyl alcohol settles out as an oil.

This is separated and distilled. Yield about 15 grams boiling at 92—96°.

$$C_2H_2O_4 + C_3H_8O_3 = C_3H_5(OH)_2.O.CO.H + H_2O + CO_2.$$
<div align="center">Glycerin monoformin.</div>

$$C_3H_5(OH)_2.O.CO.H = C_3H_5OH + H_2O + CO_2.$$
<div align="center">Allyl alcohol.</div>
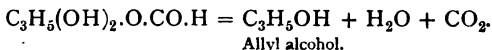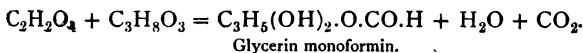
Properties.—Colourless liquid, with a pungent odour ; b.p. 96° ; sp. gr. ·858 at 0°.

Reaction.—Add bromine water to a little of the allyl alcohol. It is immediately decolourised, $C_3H_5OH + Br_2 = C_3H_5Br_2OH$.
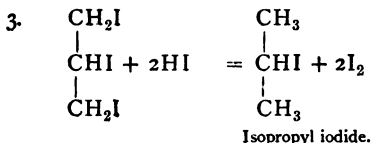
PREPARATION 28.

Isopropyl Iodide. $CH_3.CHI.CH_3$.

Markownikoff (1866), *Ann.*, 138, 364.

<div align="center">

60 grms. iodine.
40 „ glycerin.
32 „ water.
11 „ yellow phosphorus.

</div>

The iodine, glycerin, and water are placed together in a retort (250 c.c.), standing over wire-gauze and attached to a condenser and receiver. The phosphorus is cut up under a layer of water into small pieces, the size of a pea, and, with crucible tongs, dropped gradually into the retort. The introduction of the phosphorus at the beginning generally produces a violent reaction, often accompanied by a vivid flash. If no reaction occurs on adding the first few pieces of phosphorus, the retort must be warmed gently. The last two-thirds of the phosphorus may be added more quickly. The contents of the retort are now distilled as long as any oily liquid passes over. The distillate is poured back into the retort and redistilled. The liquid is then shaken up with dilute caustic soda solution in a separating-funnel, the isopropyl iodide separated, dried over calcium

COHEN'S ADV. P. O. C.

chloride, poured off and fractionated in a distilling-flask. It distils entirely at 88—89°. Yield 30—35 grams.

1. $\quad PI_3 + 3H_2O \quad = 3HI + H_3PO_3$.

2.
$$\begin{array}{ccc}
CH_2OH & & CH_2I \\
| & & | \\
CHOH + 3HI & = & CHI + 3H_2O \\
| & & | \\
CH_2OH & & CH_2I
\end{array}$$
Propenyl triiodide.

3.
$$\begin{array}{ccc}
CH_2I & & CH_3 \\
| & & | \\
CHI + 2HI & = & CHI + 2I_2 \\
| & & | \\
CH_2I & & CH_3
\end{array}$$
Isopropyl iodide.
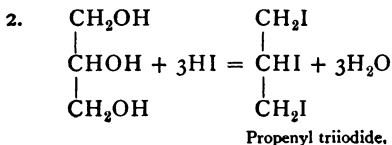
Propenyl triiodide is probably formed as an intermediate product, though it does not exist in the free state.

Properties.—Colourless liquid ; b. p. 89·5°; sp. gr. 1·744 at 0°.

PREPARATION 29.

Epichlorhydrin. $\quad CH_2Cl.CH.CH_2$
$\qquad\qquad\qquad\qquad\qquad \diagdown O \diagup$
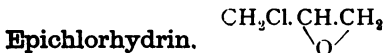
Reboul (1861), *Ann., Spl.,* 1, 221.

200 grms. glycerin.
160 c.c.   glacial acetic acid.

The glycerin, which must be dehydrated (see p. 93), is mixed with an equal volume of glacial acetic acid. Hydrochloric acid gas (see Fig. 60, p. 85) is passed into the cold liquid for about two hours, when it ceases to be absorbed. The mixture is now heated on the water-bath, and, after standing twenty-four hours, the current of gas is continued for about six hours more. The liquid is distilled with a thermometer.* Hydrochloric acid is first given off, together with acetic acid. As the temperature rises, the dichlorhydrin and acetodichlorhydrin distil. The portion distilling at 160—210°, consisting mainly of

dichlorhydrin, is collected separately and used for the preparation of epichlorhydrin. Yield of dichlorhydrin about 120 grams. Epichlorhydrin is obtained by the action of aqueous potash solution upon the dichlorhydrin. A solution of 100 grams of caustic potash in 200 c.c. of water is well cooled and poured slowly, with constant stirring, into the dichlorhydrin. Rise of temperature must be carefully avoided. The epichlorhydrin is separated from the product by adding ether, which dissolves out the epichlorhydrin. The upper layer is separated, shaken up with a little water, and again separated. It is then dehydrated over calcium chloride and decanted into a round flask. The ether is first removed on the water-bath. The residue is then fractionally distilled. This is effected by attaching a Hempel column to the flask. It consists of a wide glass tube, about 20 cm. (8 in.) long and 2 cm. inside diameter, to which a rather narrower piece is fused. A piece of copper-gauze is pushed down to the constriction, and the tube then filled with a layer of glass beads. The whole is surmounted with a T-piece, one limb of which holds the thermometer the other being attached to the condenser. The form of apparatus is shown in Fig. 65. In order that condensed liquid may not obstruct the tube, the narrow tail-piece is ground off at an angle, and a narrow sector cut out of the gauze below the beads. The liquid is now distilled, and the portion boiling at 115—125° is

FIG. 65.

epichlorhydrin, and is collected separately. The portion boiling above this temperature consists mainly of acetodichlorhydrin. Yield 25—30 grams.

$$CH_2OH.CHOH.CH_2OH + HCl = CH_2Cl.CHOH.CH_2OH + H_2O.$$
<div align="center">a-Monochlorhydrin.</div>

$$CH_2Cl.CHOH.CH_2OH + HCl = CH_2Cl.CHOH.CH_2Cl + H_2O.$$
<div align="center">aa-Dichlorhydrin.</div>

$$CH_2Cl.CHOH.CH_2Cl + KOH = CH_2.CH.CH_2Cl + KCl + H_2O.$$
<div align="center">\O/</div>

<div align="center">Epichlorhydrin.</div>

H 2
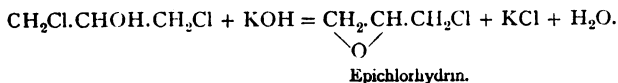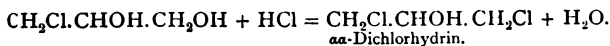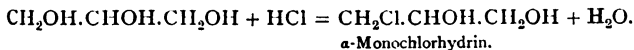
Properties.—Mobile liquid, with an ethereal smell; b.p. 117°; sp. gr. 1.203 at 0°.

Reaction.—Warm a little of the epichlorhydrin with caustic potash solution. It dissolves, forming glycerin.

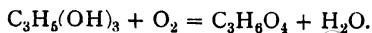<div align="center">PREPARATION 30.</div>

Glyceric Acid (Dioxypropionic Acid). $CH_2OH.CHOH.CO.OH$.

<div align="center">Debus (1858), *Ann.*, 106, 79.</div>

> 50 grms. glycerin.
> 50 ,, fuming nitric acid, sp. gr. 1.5.

The glycerin, diluted with an equal volume of water, is introduced into a tall narrow glass cylinder. The fuming nitric acid is carefully run in below the surface of the glycerin by means of a thistle-funnel, the stem of which is drawn out into a fine tube. In this way two layers are formed. The cylinder is left to stand in cold water for some time, until the two layers have diffused and formed a homogeneous liquid. The contents of two such cylinders are slowly evaporated in a large basin on the water-bath to a syrupy consistence. The residue is diluted with about 1 litre of water and the aqueous solution of glyceric acid neutralised with lead carbonate. Towards the end of the operation the liquid is heated to boiling, and filtered whilst hot. On concentrating and cooling the aqueous solution, the impure lead salt of glyceric acid is obtained. The salt, which crystallises out in crusts on the sides of the vessel to which it firmly adheres, may be detached by warming. On concentrating the mother liquors, a further quantity of crystals slowly separates out. They are filtered, and, whilst moist, finely ground and suspended in hot water (500 c.c.) and decomposed with sulphuretted hydrogen. The aqueous solution, filtered from lead sulphide, is concentrated on the water-bath, with the addition of a little animal charcoal. The liquid is again filtered when the volume has been reduced to about 200 c.c. and evaporated on the water-bath until there is no further diminution in bulk, when the acid remains in the form of a thick syrup. Yield from 100 grams of glycerin, 35—40 grams of glyceric acid.

$$C_3H_5(OH)_3 + O_2 = C_3H_6O_4 + H_2O.$$

Properties.—Strongly acid syrup, which has often a faint yellow colour and does not crystallise ; soluble in water and alcohol ; when distilled with potassium bisulphate it yields pyruvic acid.

PREPARATION 31.

Succinic Acid (Ethylenedicarboxylic Acid).
COOH.CH$_2$.CH$_2$.COOH.

Schmitt (1860), *Ann.*, 114, 106.

> 10 grms. malic acid.
> 30 „ hydriodic acid.
> 2 „ red phosphorus.

The hydriodic acid is conveniently prepared, according to Gattermann, as follows : —A small round flask (100 c.c.) is provided with a tap-funnel and delivery-tube, the latter being attached to a **U**-tube as shown in Fig. 66. The **U**-tube is filled with broken glass or pot, which has been coated with amorphous phosphorus by rubbing it in the phosphorus slightly moistened with water. The flask is first detached from the **U**-tube and funnel, and 44 grams of iodine introduced.*

FIG. 66.

Four grams of yellow phosphorus, cut in small pieces, are then added. The phosphorus must be cut under water, brought on to filter-paper with crucible tongs, pressed for a moment, and transferred with tongs to the flask. Each piece of phosphorus as it drops in produces a flash. When the phosphorus has been added a dark coloured liquid is obtained, which solidifies on cooling, and consists of PI$_3$. The flask, when cold, is closed with its cork, and the delivery tube from the **U**-tube is inserted loosely into the neck of a small flask containing 50 c.c. of water, so that the open end of the delivery-tube is above the surface of the water. It is kept in position by a wedge of cork fixed in the
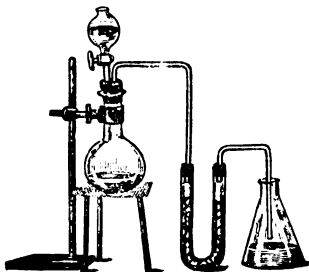
neck. Ten c.c. of water are now added gradually from the tap-funnel. Hydriodic acid is evolved, and, after being freed from iodine in the **U**-tube, is absorbed by the water. When the water has been added, the liquid is gently heated over a small flame until no more fumes issue from the delivery-tube. The aqueous solution of hydriodic acid is distilled with a thermometer, and the portion boiling at 125°and above is collected separately. It consists of strong hydriodic acid solution, containing about 57 per cent. of HI. The malic acid is dissolved in the hydriodic acid and poured into a stout-walled tube for sealing. The red phosphorus is added, and the tube sealed in the usual way (see p. 22). It is heated in the tube-furnace for six hours to 120°. On removing the tube it is found to be filled with crystals of succinic acid mixed with iodine. The contents are poured into a basin and evaporated to dryness on the water-bath. The residue, when cold, is stirred with a little chloroform to dissolve the free iodine, which is then decanted, and the process repeated if necessary. After warming to drive off the chloroform, the substance is dissolved in hot water and set aside to crystallise. Succinic acid crystallises in long prisms. Yield 5 grams.

$$COOH.CHOH.CH_2.COOH + 2HI = COOH.CH_2.CH_2.COOH + H_2O + I_2.$$
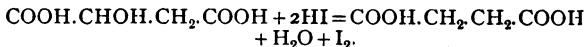
Properties.—Colourless prisms ; m.p. 180°. On distillation, the acid loses water and is converted into the anhydride.

Reaction.—1. Make a neutral solution by boiling with an excess of ammonia, and add to one portion calcium chloride ; no precipitate is formed ; to another portion add a drop or two of ferric chloride ; a brown precipitate of ferric succinate is thrown down.

Tartaric Acid (Dioxysuccinic Acid). $\begin{array}{c} CH(OH).COOH \\ | \\ CH(OH).COOH \end{array}$
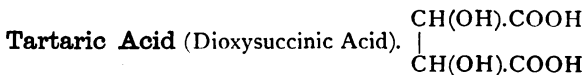
Scheele (1769).

The acid potassium or calcium tartrates are found in many plants ; but the chief source of tartaric acid is the impure acid potassium salt, which separates out as wine-lees, or argol from grape-juice in process of fermentation.

Properties. — The acid crystallises in monoclinic prisms, soluble in alcohol and water, but not in ether. It turns the plane of polarisation to the right; m.p. 167—170°. Heated with water to 165° it forms mainly mesotartaric acid; at 175° it gives more racemic acid.

Reactions.—1. Heat a crystal of the acid. It gives an odour resembling burnt sugar. Carefully neutralise a solution of tartaric acid with caustic soda, and make the following tests :—

2. Add calcium chloride and stir with a glass rod. A crystalline precipitate of calcium tartrate, $C_4H_4O_6Ca + 4H_2O$, is formed which dissolves in acetic acid and caustic alkalis. Repeat the foregoing test, but add a few drops of acetic acid before the calcium chloride. There is no precipitate. Calcium sulphate also gives no precipitate with tartaric acid or neutral tartrates, (compare reactions for oxalic acid, p. 89).

3. Add silver nitrate solution. The white precipitate is the silver salt. Add two or three drops of dilute ammonia until the precipitate is nearly dissolved, and place the test-tube in a beaker of hot water. A silver mirror will be deposited.

4. Add a few drops of acetic acid and a little ammonium or potassium acetate solution to a moderately strong solution of tartaric acid or a neutral tartrate. On stirring with a glass rod, the acid potassium or ammonium tartrate will be precipitated.

<div align="center">PREPARATION 32.</div>

Ethyl Tartrate. $$\begin{array}{l} CH(OH).CO.OC_2H_5 \\ | \\ CH(OH).CO.OC_2H_5. \end{array}$$
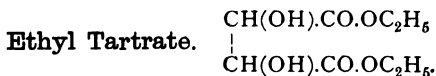
<div align="center">Anschütz, Pictet (1880), *Ber.*, 13, 1176.</div>

<div align="center">30 grms. tartaric acid.
160 c.c. absolute alcohol.</div>

The tartaric acid is finely powdered and mixed with half the above quantity (80 c.c.) of absolute alcohol. The mixture is heated on the water-bath with upright condenser until dissolved. The flask is immersed in cold water, and the well-cooled solution saturated with dry hydrochloric acid gas (prepared in the usual way by dropping conc. sulphuric acid into conc. hydrochloric acid see Fig. 60 p. 85). After standing for an

hour or two (or preferably overnight), the hydrochloric acid, excess of alcohol and water are expelled by evacuating the flask and distilling *in vacuo* on the water-bath.   The remaining half of the alcohol is added to the residue, and the mixture again saturated in the cold with hydrochloric acid gas. After standing, the acid, alcohol and water are removed as before, and the residue fractionated from an oil or metal bath *in vacuo*.   The ethyl tartrate distils as a clear viscid liquid.   After a second distillation *in vacuo* the substance is pure.

At 11 mm. it boils at 155°.
„ 20 „   „   „   164°.

The yield is 80 per cent. of the theory.

Determination of Rotatory Power.—The rotatory power of ethyl tartrate, which is an optically active substance, is determined by means of a polarimeter.   One of these instruments known as Laurent's polarimeter is shown in Figs. 67 and 68.

The monochromatic light of a sodium flame is used in these determinations and is obtained by suspending in a Bunsen flame a platinum wire basket containing fused sodium chloride or the more volatile bromide.   The latter gives a brighter flame, but the basket requires replenishing more frequently.   The light from the flame passes through a cell B, containing a solution of potassium bichromate (or a crystal of this substance), which deprives it of blue or violet rays.   It then passes through the polarising nicol prism P.   A plate of quartz cut parallel to the optic axis covers half the opening D, and is of such a thickness that it produces a difference of a half-wave length (or an exact odd multiple of a half-wave length) between the two rays, which it gives by double refraction.   The light then passes through the substance placed in the tube T and entering at E strikes the analysing nicol N.   The telescope OH is focussed on the edge of the quartz plate at D.   When N is turned, a pointer moves over the graduated circle C and its position can be read by means of the lens L.

The Theory of the Instrument may be explained as follows :—If, after passing through the nicol P, the plane of vibration is in the direction OB, Fig. 69 *a*, then in the half of the field to the right, uncovered by the quartz plate, it passes on un-
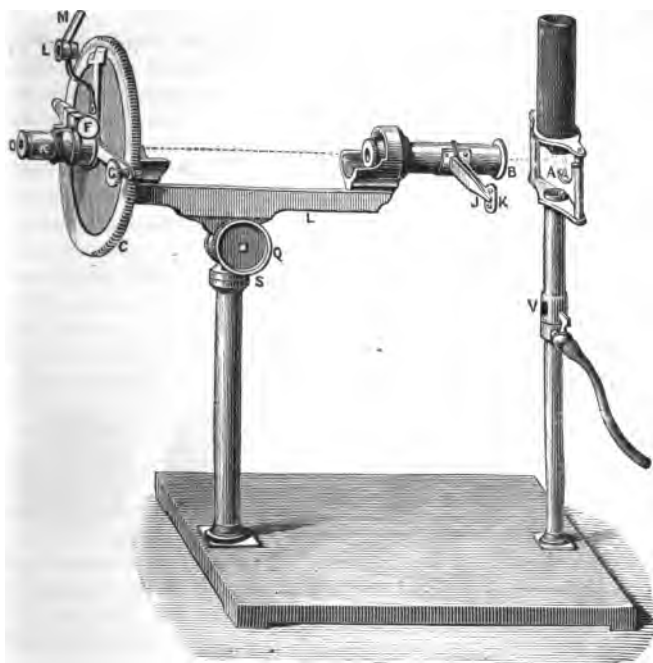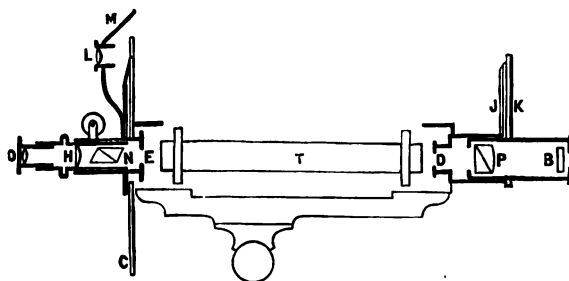
FIG. 67.

FIG. 68.

changed. When it strikes the quartz the ray is broken up into the two components Oy and Ox. These traverse the quartz with different velocities, and since one ray is retarded half a wave-length in respect of the other, the vibration of one component will be represented by Oy, but the other must be represented by Ox' instead of Ox. These two combine on emerging to a plane polarised ray vibrating in the direction OB' so that the angle AOB' is equal to the angle AOB.

If now (the tube containing water or other non-rotating liquid) the nicol N be so placed that it is parallel to nicol P, then the light, in the half of the field to the right, will pass through unchanged, but only a portion of the light which has
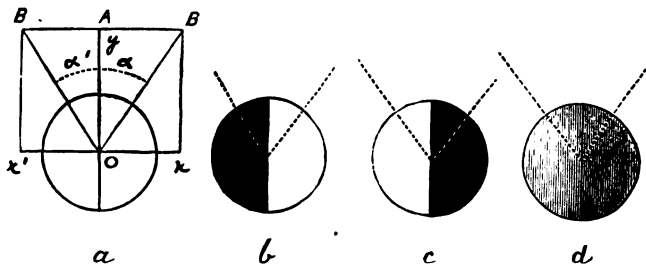
passed through the quartz diaphragm with its plane of vibration in the direction OB', will pass through N and consequently there will be different intensities of illumination in the two halves of the field, Fig. 69 b (if the angle a is 45° then the angle BOB will be 90°, and the light in the left half of the field will be completely obscured). Similarly if the plane of the nicol N be made parallel to OB' there will be a greater intensity of illumination in the left half of the field, Fig. 69 c. Between the two positions of the nicol N there must necessarily be one which gives uniform illumination of the whole field, and this is the zero point of the instrument, Fig 69 d.

If the tube T, containing the active substance, be interposed between the two nicols, then both rays OB and OB' will be rotated through equal angles, and to re-establish uniform

illumination in the two halves of the field, the nicol N must be turned through an angle equal to the angle of rotation, which is then measured on the divided circle.

When the angle a is small, *i.e.* when the plane of vibration of the polarised light is almost parallel to the optic axis of the quartz, the greatest degree of sensitiveness is attained, for then a very small change in the position of N causes a great difference in the respective illuminations in the two halves of the field. As a increases, the sensitiveness diminishes, but a greater total intensity of illumination is obtained. By moving J (Fig. 67) the position of the nicol P may be altered. For clear colourless liquids the angle a may be made comparatively small ; but in the case of coloured liquids it is necessary to have a larger, and so obtain a greater intensity of light at the cost of sensitiveness.

Calculation of Results ; Homogeneous Liquids.—The angle of rotation, represented by a_D (for sodium light), varies with the length of the column of substance through which the light passes. As unit of length one decimetre has been chosen. The angle also varies with the temperature, which must consequently be determined for each observation.

For the comparison of the rotary power of different substances, use is made of the constant *specific rotation*, which may be defined as the angle of rotation, produced by 1 gram of active substance in 1 c.c. by a layer 1 dm. in length. This is obtained by dividing the observed angle of rotation by the product of the length in decimetres, and the density of the substance at the temperature at which the observation was made.

$$[a]_D^t = \frac{a_D^t}{l \times d}$$

Molecular Rotation is the above quantity multiplied by the molecular weight M of the compound, and divided by 100 to avoid unwieldy numbers, and is represented thus—

$$[M]_D^t = \frac{[a]_D^t \times M}{100}$$

It expresses the angle of rotation of 1 mm. of active substance containing 1 gram-molecule in 1 c.c.

Rotation of Ethyl Tartrate.—Fill a 200 mm. polarimeter-tube with the tartrate prepared. Whilst it is settling determine the zero of the instrument, and if it does not coincide with the zero of the graduated circle, a corresponding correction must be introduced in the subsequent observations. The tube is then placed in the instrument, and the angle of rotation determined by turning the analyser N until equality of illumination is established in the two halves of the field. In making polarimetric observations reliance should not be placed on a single setting of the instrument, but at least five or six readings should be made, which, with a good instrument, should not differ by more than four or five minutes. The temperature at the time of observation must be noted, and the density determined either at that temperature or at two or three other temperatures, and the required density found by extrapolation.

Example : —

Temp.	Length.	a	d	$[a]_D$
$20°$	199·85 mm.	18° 28′	1·2059	7·66

$$[a]_D^{20} = 7·66°$$
$$[a]_D^{18} = 7·47°$$
$\Big\}$ Anschütz, Pictet, *Ber.*, 13. 1177.

$$[a]_D^{16} = 7·27°$$
$$[a]_D^{14} = 7·07°$$
$$[a]_D^{12} = 6·86°$$
$$[a]_D^{10} = 6·66°$$
$\Big\}$ By extrapolation.

Rotation of Tartaric Acid.—The specific rotation of a dissolved substance can be calculated from the rotation of the solution if the concentration is known. The formula to be used for this purpose is :—

$$[a]_D = \frac{100 a_D}{l.\ c.}$$

where a is the angle of rotation of solution, l the length of the tube, and c the concentration, *i.e.*, the weight in grams of the dissolved substance contained in 100 c.c. of solution. The formula $[a]_D = \frac{100 a_D}{l\ p\ d}$ may also be used (it is, in fact, identical), where p is the percentage (by weight) of substance in solution,

and d the density of the solution. The specific rotation of dissolved substances varies with the concentration and with the temperature.

Heat some tartaric acid in an air-bath to 110°, until it is quite dry. Weigh accurately about 20 grams of the dry acid and dissolve in water; then make up the solution to exactly 100 c.c. Determine the rotation of the solution in a 200 mm. tube, and note the temperature at which the observation is made.

Take 50 c.c. of the solution and dilute it to 100 c.c. Determine the rotation of this solution *at the same temperature* as that at which the first rotation was observed.

Dilute 50 c.c. of the second solution to 100 c.c., and again determine the rotation at the same temperature.

The same process can be repeated once or twice more. Calculate the specific rotation of the tartaric acid, using the first formula. Plot the results on squared paper, making the ordinates specific rotation and the abscissae concentration.

Example :—

Temp.	Concentration.	Length of tube.	Angle of Rotation.	Spec. Rot. $\frac{100\alpha}{l.c.}$
10°	40	200 mm.	6°	+ 7·5°
10°	20	,,	3° 59′	+ 9·96°
10°	10	,,	2° 11′	+ 10·91°

(Krecke, *Bischoff, Stereochemie*, p. 228.)

The following table shows the influences of temperature on the specific rotation of an aqueous solution containing 20 grams of tartaric acid in 100 c.c.

| Temp.	Length of tube.	Angle of Rotation	Specific Rotation.
0°	200 mm.	3° 28′	+ 8·66°
10°	,,	3° 59′	+ 9·96°
20°	,,	4° 38′	+ 11·57°
40°	,,	5° 28′	+ 13·66°
60°	,,	6° 28′	+ 16·16°
80°	,,	7° 21′	+ 18·38°
100°	,,	8° 36′	+ 21·50°

(Thomsen, *J. Pr. Ch.* [2] 32, 211.)

PREPARATION 33.

Pyruvic Acid. $CH_3.CO.CO.OH$.

Doebner (1887), *Ann.*, 242, 268.
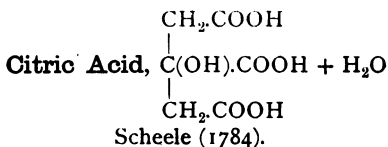
200 grms. potassium bisulphate.
100 „ tartaric acid.

The potassium bisulphate and tartaric acid must be finely powdered and intimately mixed. The mixture is distilled in a round flask (1 litre), attached to a moderately long condenser-tube, from a paraffin bath heated to 220°.* The mass at first froths up, and it is necessary to interrupt the heating when the flask is not more than half full of froth, as otherwise it may boil over. When the temperature of the bath has fallen to about 120°, the heating may be recommenced. The distillation is carried on until no more liquid distils. The distillate, which consists of water and pyruvic acid, and has a yellow colour, is fractionated *in vacuo*. It is collected at 68—70° at a pressure of 20 mm., and is quite colourless. Yield 15—20 grams. It may be fractionated at the ordinary pressure, but is difficult to obtain colourless in this way.

$$CO.OH.CHOH.CHOH.COOH = CH_3.CO.COOH + CO_2 + H_2O.$$
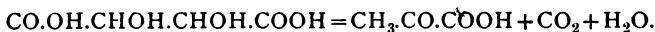
Properties.—Colourless liquid ; b.p. 165° at atmospheric pressure ; m.p. 10—11° ; polymerises on keeping.

Reaction.—Dissolve a drop of phenylhydrazine in two drops of glacial acetic acid, dilute with about 1 c.c. of water, and add a drop of pyruvic acid. A yellow crystalline precipitate of the phenylhydrazone $CH_3.C:(N.NH.C_6H_5).CO.OH$ is formed.

$$\text{Citric Acid,} \quad \begin{array}{c} CH_2.COOH \\ | \\ C(OH).COOH \\ | \\ CH_2.COOH \end{array} + H_2O$$

Scheele (1784).

Citric acid occurs in the free state, as well as in the form of the calcium and potassium salts, associated with malic and tar-

taric acid, in many plants.   It is prepared principally from lemon juice, from which it is precipitated as the calcium salt on boiling with chalk.

Properties.—The acid, which contains 1 molecule of water, crystallises in prisms ; soluble in water, alcohol, and also moderately soluble in ether ; m.p. 100°.   The anhydrous acid melts at 153—154°.

Reactions.—1. Heat a little of the acid and notice the irritating vapours.

Make a neutral solution of sodium citrate by adding caustic soda to a solution of the acid.

2. Add lime water.   There is no precipitate of the calcium salt, $(C_6H_5O_7)_2Ca_3 + 4H_2O$, until the solution is boiled.

3. Add calcium chloride solution and .boil, and, to another portion, silver nitrate solution.   Note the results and compare the reactions with those of tartaric acid (p. 102).

PREPARATION 34.

Citraconic and Mesaconic Acid.

(Methyl fumaric and Methyl maleic acid).
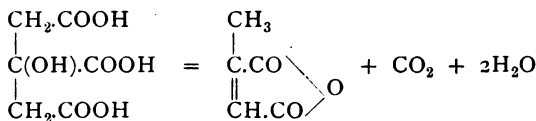
$$CH_3.C(COOH) : CH(COOH).$$
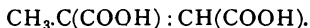
Kekulé, *Lehrbuch*, 2, 319 ; Fittig, (1877), *Ann.*, 188, 73.

250 grms. citric acid (crystallised).

Heat the crystallised citric acid, without powdering, in a porcelain basin to a temperature not exceeding 150°.   The water of crystallisation is expelled, and the crystals become pasty and then fluid.   When cold, the solid mass is removed from the basin by gently warming, and is coarsely powdered.   The anhydrous acid is *rapidly* distilled in portions of 100 grams, from a retort (250 c.c.) with bent neck (see Fig. 18, p. 20), fitted to a condenser, the receiver being a separating funnel.   The distillate consists of two layers.   The lower layer of impure citraconic anhydride is run off, and the upper layer, consisting of water and citraconic acid, is fractionated, the portion distilling at 190—210° being collected and mixed with the previous lower layer.

The citraconic anhydride is now distilled *in vacuo* and col-

lected at 110—114° under a pressure of 30 mm.   Yield 30—35 grams.

$$
\begin{array}{ccc}
CH_2.COOH & & CH_3 \\
| & & | \\
C(OH).COOH & = & C.CO \\
| & & \| \quad\quad O \\
CH_2.COOH & & CH.CO
\end{array}
\quad + CO_2 + 2H_2O
$$

Properties.—Colourless liquid ; b.p. 213—214° (ordinary pressure).   To convert the anhydride into citraconic acid the calculated quantity of water is added (1 mol. acid : 1 mol. water), and the mixture well stirred.   The whole solidifies, on standing, to a mass of colourless crystals of citraconic acid, which are dried on a porous plate ; m.p. 84—86°.

Mesaconic Acid.—To a saturated solution of citraconic acid in ether (4 parts citraconic acid require about 5 parts of anhydrous ether), about 1 part of chloroform is added, and a few drops of a moderately strong solution of bromine in chloroform. The mixture is placed in strong sunlight, when mesaconic acid, which is insoluble in ether and chloroform, begins at once to deposit on the side of the vessel nearest the light.   Drops of bromine are added from time to time until no further precipitation occurs.   The pasty mass is then filtered, washed with ether, and dried on a porous plate.   Yield 73 per cent of the citraconic acid ; m.p. 199°.   (Jacobson.)

<p style="text-align:center">PREPARATION 35.</p>

<p style="text-align:center">Urea (Carbamide). $CO\begin{cases} NH_2 \\ NH_2 \end{cases}$</p>
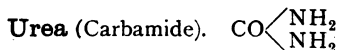
Wöhler (1828), *Pogg. Ann.*, 12, 253 ; Clemm (1848), *Ann.*, 66, 382.

> 50 grms. potassium cyanide (98—99 per cent.).
> 140   „   red oxide of lead.
> 50   „   ammonium sulphate.

The potassium cyanide is heated in an iron dish over the blow-pipe or large burner until it fuses quietly without the application of too strong a heat.   To the liquid mass 140 grams of red oxide of lead are gradually added in small quantities and stirred in, and the whole again fused for a short time.   The dark

coloured liquid mass is poured out on to an iron plate and allowed to cool. It solidifies and is powdered and separated from the solid cake of metallic lead. 200 c.c. of cold water are poured on to the crude cyanate, and, after standing an hour, filtered through a fluted-filter and washed with a little cold water. A concentrated solution of 50 grams of ammonium sulphate is immediately added to the filtrate, which is evaporated to dryness on the water-bath, the mass being stirred occasionally to prevent the formation of a surface crust. The cooled residue is powdered and the urea extracted by boiling, using an upright condenser, with small quantities of methylated spirit on the water-bath, until the extract leaves only a small residue on evaporation on a watch-glass. The greater part of the alcohol is distilled off on the water-bath, and the residue poured out into a beaker to crystallise. Yield about 15 grams.

1. $4KCN + Pb_3O_4 = 4CONK + 3Pb$
2. $(NH_4)_2SO_4 + 2CONK = 2CON.NH_4 + K_2SO_4$
3. $CON.NH_4 = CO(NH_2)_2$

Properties.—Colourless prisms; m.p. 131°; very soluble in water; soluble in hot alcohol.

Reactions.—1. Add to a strong solution of urea in water, a drop of concentrated nitric acid, and to another portion a concentrated solution of oxalic acid; the crystalline nitrate $CO(NH_2)_2$ HNO_3 and oxalate $(.CO(NH_2)_2)_2C_2H_2O_4$ are deposited.

2. Melt a few crystals of urea over a small flame and heat gently for a minute, so that bubbles of gas are slowly evolved. Cool and add a few drops of water, then a drop of copper sulphate solution, and finally a few drops of caustic soda. A violet or pink colouration is produced, depending upon the quantity of *biuret* formed.

$$2CO(NH_2)_2 = NH\!\!<\!\!{CO.NH_2 \atop CO.NH_2} + NH_3.$$
Biuret.
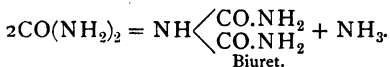
3. Add a few drops of sodium hypochlorite, or hypobromite, to solution of urea in water. Nitrogen is given off, $CO(NH_2)_2 + 3NaOCl = N_2 + 2H_2O + 3NaCl + CO_2$ (which dissolves in the alkaline solution).

4. Heat a little urea with soda-lime. Ammonia is evolved.

<div align="center">

PREPARATION 36.

Thiocarbamide (Thiourea). $SC\big\langle{}^{NH_2}_{NH_2}$.

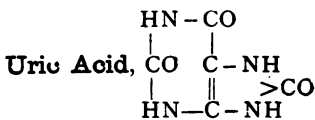</div>

Reynolds (1869), *Chem. Soc. J.*, 22, 1 ; Volhard (1874), *J. Prakt. Chem.* (2), 9, 10.

<div align="center">

50 grms. ammonium thiocyanate.

</div>

The ammonium thiocyanate is melted in a round flask on the oil-bath, and kept at a temperature at which the mass remains just liquid (140—145°) for 5—6 hours. The cooled melt is powdered and ground with half its weight of cold water, which dissolves unchanged ammonium thiocyanate, but little of the thiourea. By dissolving the residue in a little hot water, pure thiourea is obtained, on cooling, in colourless, silky needles. Yield 7—8 grams.

$$CNS.NH_4 = CS(NH_2)_2$$
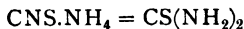
Properties—Colourless, rhombic prisms (from dilute aqueous solution), long silky needles (from concentrated solutions) ; m. p. 175°. Very slightly soluble in cold water (1 part of thiourea dissolves in about 11 parts of water at the ordinary temperature).

<div align="center">

$$\text{Uric Acid,} \quad \begin{matrix} HN - CO \\ | \qquad | \\ CO \quad C-NH \\ | \quad\; \| \quad\; >CO \\ HN-C-NH \end{matrix}$$

Scheele (1776).

</div>

Uric acid is a product of the metabolism of the animal organism. It is usually prepared from guano, which is treated first with dilute hydrochloric acid to remove phosphate of calcium. The uric acid is then dissolved out with hot caustic soda. The clear alkaline solution is precipitated with acid.

Properties.—Uric acid forms microscopic crystals of a characteristic shape. It is insoluble in water, but dissolves in the presence of many organic substances. On dry distillation, it yields ammonia, cyanuric acid, and urea.

Reactions.—Evaporate a little of the acid with a few c.c. of dilute nitric acid to dryness on the water-bath. An orange or red residue remains. On cooling, add ammonia. A fine purple colour is produced (murexide test); see also Reaction for alloxan (p. 116).

PREPARATION 37.

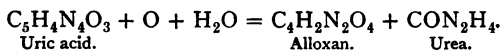### Alloxantin. $C_8H_4N_4O_7 + 3H_2O$.

Liebig, Wöhler (1838), *Ann.*, **26**, 262.

10 grms. uric acid.
20 „ conc. hydrochloric acid diluted with an equal weight of water.
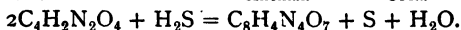2½ „ potassium chlorate.

The hydrochloric acid is poured over the uric acid. The mixture is heated to 35°, and the potassium chlorate, finely powdered, is added in small quantities at a time with constant shaking. When about two grams of the chlorate have been added, the uric acid will have nearly dissolved, and the liquid has a faint yellow colour. It is diluted with double its volume of water, allowed to stand for about an hour, and filtered. The filtrate is saturated with sulphuretted hydrogen, and yields, after being left for 12 hours, crystalline crusts, often of a reddish tint, of alloxantin mixed with sulphur. It is filtered and washed with cold water, and the alloxantin dissolved in a small quantity of hot water, and filtered from the residue of sulphur. On cooling the filtrate, colourless crystals separate out. Yield 7—8 grams.

$$C_5H_4N_4O_3 + O + H_2O = C_4H_2N_2O_4 + CON_2H_4.$$
$$\text{Uric acid.} \qquad\qquad \text{Alloxan.} \qquad \text{Urea.}$$
$$2C_4H_2N_2O_4 + H_2S = C_8H_4N_4O_7 + S + H_2O.$$
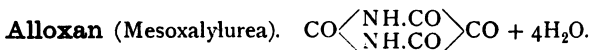$$\text{Alloxantin.}$$

Properties.—Hard, colourless crystals, slightly soluble in cold, more readily in hot water.

Reactions.—1. Add to the solution of alloxantin a little baryta water; a violet colouration is produced.

2. Add ammonio-silver nitrate solution and warm ; metallic silver is deposited.

3. Boil the solution with mercuric oxide ; a violet solution of murexide is formed.

PREPARATION 38.

Alloxan (Mesoxalylurea). $CO\left\langle\begin{matrix}NH.CO\\NH.CO\end{matrix}\right\rangle CO + 4H_2O.$

Liebig, Wöhler (1838), *Ann.*, 26, 256.

5 grms. alloxantin.
5 „   conc. nitric acid (sp. gr. 1·4).
10 „   fuming   „   (sp. gr. 1·5).

The finely powdered alloxantin is added to a mixture of the strong and fuming nitric acid, and left to stand. Slight evolution of nitrous fumes occurs, and the alloxantin, which at first remains at the bottom of the vessel, slowly changes into the more bulky crystals of alloxan, which gradually fill the liquid. The reaction lasts about two days, and is complete when a sample dissolves readily and completely in cold water. The crystalline mass is spread upon a porous plate, thoroughly dried in the air, and freed from traces of nitric acid by heating in a basin on the water-bath, until the smell of the acid disappears. Alloxan may be obtained in large crystals by dissolving the dry product in the smallest quantity of hot water, and allowing the solution to evaporate slowly in a desiccator over sulphuric acid. The crystals are liable to effloresce.

$$C_8H_4N_4O_7 + O = 2C_4H_2N_2O_4.$$
<div style="text-align:center">Alloxantin.   Alloxan.</div>
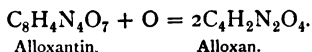
Properties.—Colourless crystals, containing 4 molecules of water of crystallisation.

Reactions.—1. A small quantity of the alloxan solution is evaporated to dryness on the water-bath in a porcelain basin. A reddish residue is left, which turns purple on the addition of ammonia (murexide).

PREPARATION 39.

Caffeine (Trimethyl xanthine).

$$CH_3.N - CO$$
$$CO \quad C - N(CH_3)$$
$$CH_3.N - C - N \diagup CH.$$
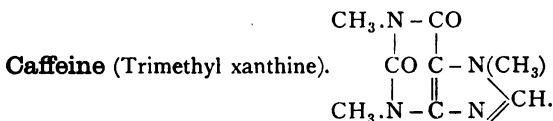
100 grms. tea.

Digest the tea with 500 c.c. boiling water for a quarter of an hour, and filter through cloth into a basin placed over a ring burner (see p. 95), so that the liquid in the filter is kept hot. Moderately fine unsized cotton cloth is used, and is wetted and stretched on a wooden frame as shown in Fig. 70. Wash with a further 250 c.c. of boiling water. Add to the filtrate a solution of basic lead acetate (made by boiling acetate of lead solution with excess of litharge, and then filtering) until no more
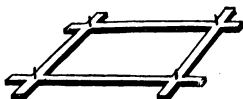

FIG. 70.

precipitate is formed. Filter hot through a large fluted-filter from precipitated albumen, and wash with water. To the boiling filtrate add dilute sulphuric acid until the lead is precipitated as sulphate. Filter or decant from the sulphate of lead, and concentrate the solution with the addition of animal charcoal to 250—300 c.c. Filter and extract the filtrate three times with small quantities (50 c.c.) of chloroform. Distil off the chloroform on the water-bath, and dissolve the residue in a small quantity of hot water. On allowing the solution to evaporate very slowly, long silky needles of caffeine separate, which may have a slightly yellow tint, in which case they should be drained, re-dissolved in water, and boiled with the addition of animal charcoal. Yield about 1·5 gram.

PREPARATION 40.

**Creatine.** $HN : C\begin{cases} N(CH_3).CH_2.CO.OH \\ NH_2 \end{cases} + H_2O$
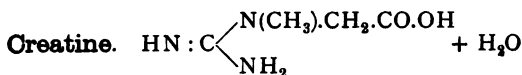
Neubauer (1861), *Ann.*, 119, 27.

500 grms. meat.

The meat, separated as far as possible from fat, is put through a sausage machine, or finely chopped and digested with ½ litre of water at 50—60°, and well stirred from time to time. It is filtered through cloth (see Fig. 70, p. 117), and is then digested with a further 250 c.c. of water in the same way, filtered, and the cloth removed from the frame and squeezed out. The filtrate is heated to boiling to coagulate the albumen, and, on cooling, filtered. Basic acetate of lead is carefully added, just sufficient to precipitate the soluble albumen. The liquid is again filtered through a fluted filter, and the lead removed with sulphuretted hydrogen, which is passed into the warm liquid. The filtrate from the sulphide of lead is concentrated to a thin syrup on the water-bath and then transferred to a vacuum desiccator, where it is left over sulphuric acid. In a short time, especially on the addition of a crystal of creatine, needle-shaped crystals begin to separate, and when no further crystallisation is observed, the crystals, which have a brown colour, are brought on to a porcelain-funnel and washed with a little methylated spirit. They are recrystallised from a little hot water, with the addition of animal charcoal. Yield about 1 gram. The filtrate from the creatine contains hypoxanthine and sarcolactic acid, but the small quantity of these two constituents render them difficult to extract.
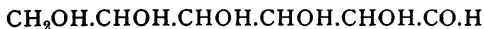
Properties.—Small rhombic prisms ; with difficulty soluble in cold water, readily soluble in hot water. On warming with alkalis, it decomposes into urea and sarcosine,

$HN : C\begin{cases} N(CH_3).CH_2.COOH \\ NH_2 \end{cases} + NaOH = CO(NH_2)_2 + NH(CH_3).CH_2.COONa.$
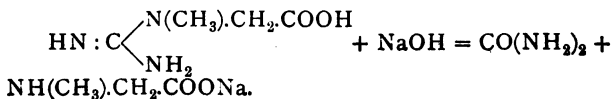
PREPARATION 41.

Grape Sugar. (Glucose, Dextrose).

Soxhlet (1880), *J. Prakt. Ch.* (2) 21, 245.

$$CH_2OH.CHOH.CHOH.CHOH.CHOH.CO.H$$

750 c.c. methylated spirit.
30 c.c. conc. hydrochloric acid.
250 grms. cane sugar.

The spirit and acid are mixed and warmed to 45—50°, whilst the finely powdered cane-sugar is gradually added and stirred. When the sugar has dissolved, the solution is cooled, and a few crystals of anhydrous grape-sugar added. On standing for a day or two, the grape-sugar deposits in the form of fine crystals, which continue to increase in quantity. When no further deposition is observed, the crystals are filtered and washed with methylated spirit. The sugar may be purified by dissolving in a little water to a syrup, and adding hot methyl alcohol until a turbidity appears. On cooling, the grape-sugar crystallises out.

$$C_{10}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$
Cane sugar.   Glucose.   Fructose.
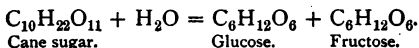
Properties.—Colourless crystals ; m.p. 146° ; soluble in hot and cold water, insoluble in alcohol.

Reactions.—1. Add to a little of the solution of glucose a few drops of caustic soda, and warm. The colour changes from yellow to brown.

2. Add to 2 or 3 c.c. of the solution, two or three drops of copper sulphate, and then caustic soda, until a clear blue solution is obtained, and heat to boiling. Red cuprous oxide is precipitated.

3. Add a few drops of glucose solution to half a test-tube of ammonio-silver nitrate solution and place the test-tube in hot water. A mirror of metallic silver is formed.

4. Dissolve about ·5 gram of glucose in 5 c.c. of water, and add a solution of phenylhydrazine acetate, made by dissolving 1 gram of phenylhydrazine in the same weight of glacial acetic acid, and diluting to 5 c.c. Mix the solutions and warm in the water-bath. In a few minutes the yellow crystalline phenyl-glucosazone (m.p. 204—205°) is deposited.

Benzene.

Pure Commercial Benzene, obtained from coal-tar naphtha, should distil within one degree (80—81°), and solidify completely when cooled to 0°. Other tests are as follows: Shaken with concentrated sulphuric acid for a few minutes, the acid should not darken, and a drop of bromine water should not be immediately decolourised. A single distillation over a few small pieces of sodium, which absorb any traces of water, is usually a sufficient purification. If the benzene impart a brown or black colour to the sulphuric acid, it must be repeatedly shaken with about 20 per cent. of the acid until the latter becomes only slightly yellow on standing. This is done in a stoppered separating funnel, and after shaking for a few minutes the mixture is allowed to settle, and the lower layer of acid drawn off. The benzene is then shaken two or three times with water to free it from acid, carefully separated from the aqueous layer, and left in contact with fused calcium chloride until the liquid becomes clear. It is then decanted, frozen in ice, and any liquid (carbon bisulphide, paraffins) carefully drained off, and the benzene finally distilled over sodium.

Properties.—Mobile, colourless liquid; m.p. 5·4°; b.p. 80·4°; sp. gr. ·874 at 20°. Coal-tar benzene usually contains a little thiophene, C_4H_4S, which may be detected by dissolving a few crystals of isatin (see p. 185) in concentrated sulphuric acid and shaking up with the benzene. If thiophene is present, a blue colour is produced (indophenin reaction).

Fractional Distillation.—It is often possible to separate almost completely by a single distillation, two liquids occurring together in a mixture when their boiling points lie widely apart. The more volatile liquid first passes over, the temperature suddenly rises, and the higher boiling liquid distils.

It is otherwise when a liquid consists of a mixture of substances boiling at temperatures not very far removed from one another, especially in the case of homologous compounds, such as occur in petroleum and coal-tar naphtha. One distillation suffices only to produce very partial separation of the different substances, a portion of the less volatile liquid being carried over in the first distillate, together with the more volatile body,
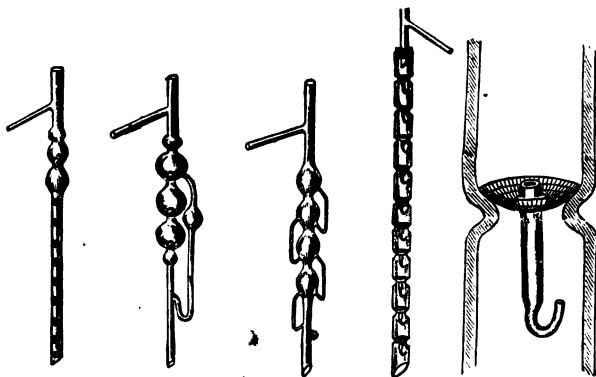

FIG. 71.   FIG. 72.   FIG. 73.   FIG. 74.   FIG. 75.

The apparatus of Linnemann, Fig. 71, contains a series of wire gauze cups ; that of Glinsky, Fig. 72, has beads at the constrictions, and a side-tube. Lebel and Henninger's apparatus, Fig. 73, has a series of bulbs connected by side-tubes. The Young and Thomas apparatus is shown in Figs. 74 and 75.

the temperature gradually rising throughout the distillation. In order to effect separation of the several substances, recourse is had to the method of fractional distillation.

The liquid is distilled in a round flask over wire-gauze or, better, in a fusible metal bath, a bit of porous pot or a coil of platinum-wire being placed in the flask to prevent bumping. The flask is surmounted with a fractionating column, in which the thermometer is fixed. Various forms of fractionating columns are used (see Figs. 71—74, and also Fig. 65, p. 99).

The effect of the column may be explained as follows : The

vapour given off from a mixture of liquids contains a larger proportion of the more volatile constituent than the liquid. If this vapour is condensed in its ascent, the vapour above this condensed liquid will be still richer in the more volatile constituent. If, by a series of constrictions or diaphragms, the condensed liquid is obstructed in its return flow, a momentary equilibrium between liquid and vapour is established at each diaphragm, and the larger the column the greater will be the amount of more volatile constituent in the last portion of vapour to undergo condensation. This passes off by the condenser and is collected in the receiver. The Hempel and Young and Thomas columns may be recommended on the ground of efficiency and ease of construction. The Hempel apparatus has already been described (see Fig. 65, p. 99). The Young and Thomas apparatus can be made out of a piece of similar wide tubing. This is constricted in the blow-pipe flame, near one end, and a piece of copper wire-gauze with a circular hole, carrying the little bent tube, is placed on the constriction (Fig. 75). A second constriction is made and another gauze diaphragm introduced. The number of diaphragms may vary from 10 to 20, according to the degree of separation required.[1]

Commercial 50 per cent. and 90 per cent. Benzene are mixtures of benzene and larger or smaller quantities of its higher boiling homologues, viz., toluene (b.p. 110°) and the xylenes (b.p. 137—143°). The constituents may be separated by fractional distillation.

Fit up an apparatus with fractionating column and distil 200 c.c. 50 per cent. or 90 per cent. benzene, at a regular speed, so that the drops falling from the end of the condenser may be readily counted. Collect the distillate between every five degrees in separate flasks. Redistil each of these fractions in order, adding the next to the residue of the previous one in the distilling-flask. Collect portions boiling below 85° and above 105°, between every two or three degrees. It will be found that by a repetition of the process the liquid is gradually separated into two large fractions, consisting chiefly of benzene and toluene, and a number of smaller intermediate fractions. The following table gives the volume in c.c., and the boiling points of the

fractions obtained by this method from 200 c.c., 50 per cent. benzene, each table denoting a complete series of fractionations, using a simple column with two bulbs.

I.

A. 71·5-85°	B. 85-90°	C. 90-95°	D. 95-100°	E. 100-105°	F. 105-110°	G. 110-115°	Residue.
19 c.c.	53 c.c.	26 c.c.	15 c.c.	13 c.c.	17 c.c.	21 c.c.	33 c.c.

II.

	A' below 79°.	B'. 79-81°	C'. 81-85°	D'. 85-105°	E'. 105-108°	F'. 108-110°	Residue.
A.	5 c.c.	...	...	...	...	...	...
Added B.	...	42 c.c.	(10 c.c.*)	...	...	...	...
Added C.	...	...	(7 c.c.*)	...	...	...	...
Added D. E.	..	...	...	50 c.c.	...	...	...
Added F.	...	..	...	...	(11 c.c.*)	...	...
Added G.	...	...	...	...	...	22 c.c.	42 c.c.
*Refractionated C'.	...	12 c.c.	7 c.c.	...	...	...	...
E'.	...	...	...	...	6 c.c.	5 c.c.	...
	5 c.c.	54 c.c.	7 c.c.	50 c.c.	6 c.c.	27 c.c.	42 c.c.

The fraction 79—81° is further purified in the manner already described.

PREPARATION 42.

Bromobenzene (Phenyl bromide). C_6H_5Br.

Cohen and Dakin (1899), *Chem. Soc. J.*, 76, 894.

> 50 grms. benzene.
> 60   „   (20 c.c.) bromine.
> 1   „   aluminum-mercury couple.

The apparatus required is shown in Fig. 58, p. 81.   The benzene is introduced into the flask, and the bromine into the tap-funnel above the condenser. The aluminium-mercury couple is prepared by pouring a saturated solution of mercuric chloride on to aluminium foil, which is cut into strips or formed into small rolls.   After about a minute, the surface of the aluminium is coated with a film of metallic mercury.   The solution is poured off, the foil well washed with water, then with alcohol, and finally with a little benzene.   This must be done as quickly as possible, and the pieces of couple dropped into the benzene in the flask.   The bromine is now added drop by drop from the tap-funnel, when a rapid evolution of hydrobromic acid occurs, the acid being absorbed by the water in the beaker.   When, in the course of about half an hour, all the bromine has been added, the contents of the flask are shaken up with dilute caustic soda solution. Sufficient alkali must be present so that an excess remains after shaking.   The lower layer is separated by means of a tap-funnel and dehydrated over calcium chloride.   When perfectly clear, the liquid is filtered into a distilling-flask (200 c.c.), and distilled over wire-gauze with a thermometer.   Unchanged benzene first passes over ; the temperature then rises rapidly, and the portion boiling at 140—170° is collected separately.   It is redistilled and collected at 150—160°.   Yield 30—35 grams.

$$C_6H_6 + Br_2 = C_6H_5Br + HBr.$$
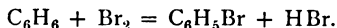
The aluminium-mercury couple acts as a " halogen carrier," but in what manner is not understood.

Properties. — Colourless   liquid ;   b.p.   154 — 155° ;   sp.   gr. 1·5176 at 0°.   The weak solution of hydrobromic acid which collects in the beaker may be concentrated by fractional distillation, as in the case of hydriodic acid (see p. 101).   It boils at 126° and contains about 47 per cent. of HBr.
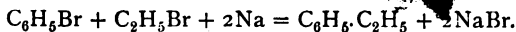
PREPARATION 43.

Ethyl Benzene. $C_6H_5.C_2H_5$.

Fittig (1864), *Ann.*, 131, 303.

60 grms. bromobenzene.
52 „ . ethyl bromide (see p. 48).
26·5 „ sodium.

A quantity of ether, which has been freed from alcohol by shaking with small quantities of brine, and dried over calcium chloride and sodium (see p. 53), is poured into a round flask (1 litre). The amount of ether should be about twice the volume of the mixed phenyl and ethyl bromides. The sodium, cut into thin slices with the sodium knife, or squeezed into fine wire, is added to the ether, and when all evolution of hydrogen has ceased, the flask is attached to an upright condenser and immersed in a vessel of ice-water. The mixture of bromo-benzene and ethyl bromide, both carefully dehydrated, is poured into the flask. The reaction is allowed to commence spontane-ously, the fact being indicated by the approach of the sodium, which becomes darker. A colour and sinks to bottom of the vessel. Although the flask is allowed to remain in the outer vessel, and is cooled by water and ice, the heat evolved often causes the ether to boil. The flask is therefore not removed until the reaction is over. It is convenient to leave it over night. The liquid is then decanted from the sodium bromide, which has a blue colour, into a distilling-flask, and rinsed out once or twice with ether. The ether is removed on the water-bath, a bit of porous pot being added, and the residue is fractionated with a Hempel column. The portion boiling at 132°—135° is collected separately. Yield 20—25 grams.

$$C_6H_5Br + C_2H_5Br + 2Na = C_6H_5.C_2H_5 + 2NaBr.$$

Properties.—Colourless liquid; b.p. 134°; sp. gr. ·8664 at 22·5°.

PREPARATION 44.

Nitrobenzene. $C_6H_5NO_2$

Mitscherlich (1834), *Ann.*, 12, 305.

> 50 grms. benzene.
> 100   „   conc. nitric acid, sp. gr. 1·4.
> 150   „   conc. sulphuric acid.

The two acids are mixed and well cooled, and then slowly added from a tap-funnel to the benzene, which is contained in a flask ($\frac{1}{2}$ litre). The contents of the flask are *well shaken* after each fresh addition. Nitrous fumes are evolved, and a considerable amount of heat developed. Care must, however, be taken that the temperature does not exceed 50°—60° by immersing the flask, if necessary, in cold water. The nitrobenzene separates out as a brown, oily layer on the surface of the acid liquid. When the acid has all been added, an operation which lasts about half an hour, the mixture is heated for about twenty minutes on the water-bath, and again well shaken. The contents of the flask on cooling, are poured into a stoppered separating-funnel, the lower layer of acid removed, and the nitrobenzene washed free from acid by shaking once with water (taken up), then with dilute carbonate of soda solution, and again with water, the oil being each time withdrawn from the bottom of the vessel. The nitrobenzene, separated as carefully as possible from water, is allowed to stand over a few pieces of fused calcium chloride, and shaken occasionally until the liquid is clear. The yellow liquid is decanted, or filtered from the calcium chloride, and distilled in a distilling-flask, with condenser tube only. At first a little benzene passes over ; the temperature then rises, and the nitrobenzene distils at 204°—207°, and is separately collected. The brown residue consists of dinitrobenzene, the quantity depending upon whether the temperature during nitration has been allowed to rise too high. Yield about 60 grams.

$$C_6H_6 + HO.NO_2 = C_6H_5NO_2 + H_2O$$
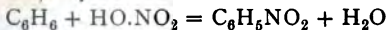
The function of the sulphuric acid is that of a dehydrating agent taking up the water formed in the reaction.

Properties.—Light yellow liquid, with a smell of bitter almonds ; b.p. 206°—207°, sp. gr. 1·208 at 15° ; m.p. 3° ; insoluble in water, soluble in alcohol, ether, and benzene.

Reaction.—Pour a drop of nitrobenzene into a test-tube with 1 c.c. water and 1 c.c. glacial acetic acid. Add a little zinc-dust on the point of a penknife, and warm for a minute. Dilute with a few c.c. of water, and add caustic soda solution until alkaline, and pour a few drops into a test-tube half filled with sodium hypochlorite solution. A violet colouration, which gradually fades, is produced, due to the presence of aniline (see p. 130).

PREPARATION 45.

Azoxybenzene. $C_6H_5N-N.C_6H_5$
                         $\diagdown O \diagup$

about
.lute with ether (1882), *Ber.*, 15, 865.
Colourless pl   rms. methyl alcohol.
$C_6H_5NH.NH$,, sodium.
,, nitrobenzene.

Attach   dens r to a round flask (½ litre). Pour in the m   cohol and add the sodium in small pieces, 2—3 gra   ine (A   time. A good stream of water should pass through th   nser, but otherwise the flask need not be cooled. Wh the sodium has dissolved, the nitrobenzene is introduced, and the mixture boiled on a water-bath three to four hours. The methyl alcohol is then distilled off in the water-bath. As the liquid is liable to bump, owing to the separation of solid matter, it is advisable to add a few bits of pot. When no more alcohol distils, the residue is poured into a beaker of water and rinsed out. A dark-coloured oil is deposited, which soon solidifies, and is then washed by decantation, and pressed on a porous plate. Yield about 23 grms. It is recrystallised, when dry, from ligroin, in which it rather soluble.

$$4C_6H_5NO_2 + 3NaOCH_3 = 2C_6H_5N - N.C_6H_5 + 3H_3CO.ONa$$
$$\diagdown O \diagup$$
$$+ 3H_2O.$$
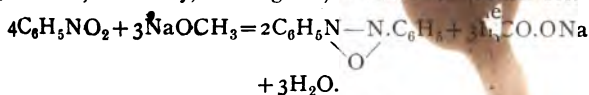
*Properties.*—Yellow needles ; m.p. 36°.

PREPARATION 46.

Azobenzene. $C_6H_5N:N.C_6H_5.$

Mitscherlich (1834), *Ann.*, 12, 311.

5 grms. azoxybenzene.
15 „   iron filings.

The azoxybenzene and iron filings, both of which must be carefully dried on the water-bath, are powdered together and distilled from a small retort, which is conveniently made by blowing a large bulb on the end of a piece of rather wide tubing $1\frac{1}{2}$ cm. inside diameter, and then allowing the bulb, whilst hot, to bend over. The mixture is carefully heated, the burner being moved about until the contents are thoroughly hot, and then the mixture is more strongly heated until nothing further distils. The distillate, which is a dark-red mass, is washed with a little dilute hydrochloric acid and water, and then pressed on a porous plate. It is recrystallised from ligroin, in which it is very soluble.

$$C_6H_5N\text{--}N C_6H_5 + Fe = C_6H_5N:N C_6H_5 + FeO.$$
$$O$$
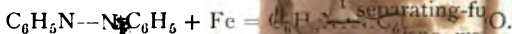
Properties.—Red plates ; m.p. 68° ; b.p. 293°.

PREPARATION 47.

Hydrazobenzene (Diphenylhydrazine). $C_6H_5NH.NHC_6H_5.$

Meyer and Jacobson, *Lehrb. der Org. Chem.*, 2, 275.

5 grms. azobenzene.
50 „   absolute alcohol.
2 „   caustic soda (in 6 c.c. water).
$7\frac{1}{2}$ „   zinc dust.

The azobenzene is dissolved in alcohol, and the caustic soda added. The mixture is heated on the water-bath with upright condenser ; zinc-dust is then added in small portions at a time, until the solution is decolourised ($7\frac{1}{2}$ grams). It is then filtered

at the pump and washed with a little alcohol. Water, into which a little sulphur dioxide has been passed, is then added cautiously until a cloudiness appears. On cooling, the hydrazo-benzene crystallises in small, colourless plates. It may be recrystallised from ligroin. As hydrazobenzene readily oxidises in air, forming azobenzene, it must be protected as far as possible during the process of filtration and crystallisation.

$$C_6H_5N:N.C_6H_5 + 2NaOH + Zn = C_6H_5NH.NHC_6H_5 + Zn(ONa)_2.$$
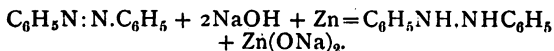
Properties.—Colourless plates ; m.p. 131°.

Reactions.—1. Heat a small quantity in a dry test-tube. Notice the colour. On cooling, add a little water and pour a few drops into sodium hypochlorite solution, $2C_6H_5NH.NHC_6H_5 = C_6H_5N:N.C_6H_5 + 2C_6H_5NH_2.$

2. Heat about $\cdot5$ gram with 2 c.c. concentrated HCl for a minute, dilute with a little water, filter, and add ammonia in excess. Colourless plates of benzidine separate.

$$C_6H_5NH.NHC_6H_5 = H_2N.C_6H_4.C_6H_4.NH_2.$$
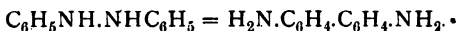
PREPARATION 48.

Aniline (Amidobenzene ; Phenylamine). $C_6H_5NH_2.$

Zinin (1842), *Ann.*, 44, 283.

50 grms. nitrobenzene.
90. ,, granulated tin.
170 c.c. conc. hydrochloric acid (sp. gr. 1·16).

Introduce the tin and nitrobenzene into a round flask ($1\frac{1}{2}$ litre), and fit it with a straight upright tube about 2 feet long (air-condenser). Heat the mixture for a few minutes on the water-bath. Then remove the flask and add the concentrated hydrochloric acid in quantities of 5—10 c.c. at a time, and shake repeatedly. The liquid should become hot and boil quietly ; but, if the action becomes too violent, it must be moderated by cooling the flask in cold water. In the course of $\frac{1}{2}$—$\frac{3}{4}$ hour all the acid should have been added ; the flask is then replaced on

the water-bath without the air-condenser, and heated for an hour or more until the reduction is complete. This is ascertained by the absence of any smell of nitrobenzene. The contents of the flask, on cooling, solidify to a crystalline mass (a double salt of stannic chloride and aniline hydrochloride). Whilst still warm, water (100 c.c.) and strong caustic soda solution (140 grams in 200 c.c. water) are added until the stannic oxide, which is first precipitated, nearly redissolves, and the liquid has a strongly alkaline reaction. If the mixture begins to boil during the addition of the caustic soda solution, it must be cooled. The aniline, which separates out as a dark-coloured oil, is distilled in steam. The apparatus is shown in Fig. 63, p. 94. The flask containing the aniline is gently heated on the sand-bath, and steam is passed in from the tin bottle. It is advisable to heat the aniline mixture nearly to its boiling-point before steam is admitted, as otherwise a large quantity of water condenses in the flask. On distillation, aniline and water collect in the receiver, the former as a colourless oil. When the distillate, as it comes over, appears clear instead of milky, the distillation is stopped. The oil is now extracted from the distillate by shaking up the liquid in a separating-funnel three times with small quantities (50 c.c.) of ether. The ethereal solution, separated as far as possible from water, is further dehydrated by adding a few pieces of solid caustic potash. The clear liquid is decanted into a distilling-flask, the potash rinsed with a little more ether, and the ether distilled off on the water-bath until nothing more passes over. The residue is then distilled over wire-gauze. Aniline distils at 181—182°, and has usually a faint amber colour. Yield, about 30 grams.

$$2C_6H_5NO_2 + 3Sn + 12HCl = 2C_6H_5NH_2 + 3SnCl_4 + 4H_2O.$$
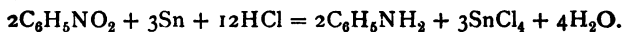
Properties.—Colourless, highly refractive liquid, which soon darkens in colour; b.p. 182°; sp. gr. 1·0265 at 15°.

Reactions.—1. Add a drop of the oil to a solution of bleaching powder or sodium hypochlorite. An intense violet colouration is produced, which gradually fades.

2. Heat a drop of the oil with a few drops of chloroform, and about 1 c.c. of alcoholic potash, in the fume-cupboard. Phenyl

carbamine is formed, which possesses an intolerable smell. (Hofmann's reaction for primary amines).

3. Add to a drop of aniline in a basin a few drops of concentrated sulphuric acid, and stir with a glass rod. Then add a few drops of potassium bichromate solution. An intense blue colour is obtained.

PREPARATION 49.

Acetanilide (Phenylacetamide). $C_6H_5.NH.CO.CH_3$.

G. Williams (1864), *Chem. Soc. J.*, (2) 106.

25 grms. aniline (freshly distilled).
30 „ glacial acetic acid.

Boil the mixture gently in a flask (250 c.c.), fitted with an air-condenser, for a day (7—8 hours). As the liquid solidifies on cooling, it is at once poured out, while hot, into a basin of cold water (500 c.c.). It is filtered and washed with cold water. Acetanilide crystallises best from hot water, in which, however, it is not very soluble. Place the moist acetanilide in a large basin, and add gradually about a litre of boiling water. If the substance does not dissolve completely on boiling, a small quantity of methylated spirit will bring it into solution. Filter through a large

FIG. 76.

fluted filter or hot-water funnel, and set the solution aside to crystallise. A hot-water funnel is shown in Fig. 76. It consists of a jacketed metal funnel with a projecting metal tube. The vessel is partly filled with water, which is boiled by placing a small burner under the end of the tube. The glass-funnel is placed within the metal-jacket. In this way the liquid is kept hot, and crystallisation in the filter is prevented. If the crystals are discoloured, they should be
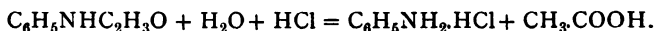
redissolved as before, and heated with a little animal charcoal (5—10 grams) for $\frac{1}{2}$ hour and then filtered. Yield, 30—35 grams.

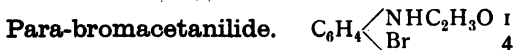$$C_6H_5NH_2 + CH_3.COOH = C_6H_5NH.CO.CH_3 + H_2O.$$
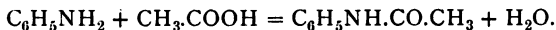
Properties.—Rhombic plates ; m.p. 112° ; b.p. 295°.

Reaction.—Introduce about ·5 gram of the substance into a test-tube, and add 3 c.c. concentrated hydrochloric acid. Boil for a minute. On diluting with water, a clear solution is obtained,

$$C_6H_5NHC_2H_3O + H_2O + HCl = C_6H_5NH_2.HCl + CH_3.COOH.$$

PREPARATION 50.

Para-bromacetanilide. $C_6H_4 \diagdown \begin{matrix} NHC_2H_3O & 1 \\ Br & 4 \end{matrix}$

Remmers (1874), *Ber.*, **7**, 346.

5 grms. acetanilide.
25 c.c. glacial acetic acid.
6 grms. bromine.

Dissolve the acetanilide in the acetic acid in a flask ($\frac{1}{2}$ litre), and add gradually the bromine, dissolved in about twice its volume of glacial acetic acid, and shake well. When the bromine has been added, let the mixture stand $\frac{1}{4}$ hour and then pour into 200 c.c. water and rinse out with water. Filter the crystalline precipitate at the pump and wash three or four times with water. Press it well down and let it drain. Dissolve the moist substance in methylated spirit (about 60 c.c.) and pour into a beaker to crystallise. Filter the crystals, wash with a little dilute spirit, and dry on filter paper. Yield, 6—7 grams.

$$C_6H_5NH.C_2H_3O + Br_2 = C_6H_4Br.NH.C_2H_3O + HBr.$$
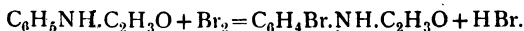
Properties.—Colourless needles ; m.p. 165 — 166°. On hydrolysis with concentrated hydrochloric acid, para-bromaniline is formed (see above reaction for acetanilide).

PREPARATION 51.

Meta-dinitrobenzene. $C_6H_4 \begin{smallmatrix} NO_2 & 1 \\ NO_2 & 3 \end{smallmatrix}$

Deville (1841), *Ann. Ch. Phys.* (3), 3, 187 ; Hofmann, Muspratt (1846), *Ann.*, 57, 214.

    30 grms. nitrobenzene.
    35   ,,   (24 c.c.) fuming nitric acid ; sp. gr. 1·5.
    35   ,,   (20 c.c.) conc. sulphuric acid.

The acids are mixed in a flask (500 c.c.), and the nitrobenzene added in portions of 5—10 c.c. at a time. Heat is evolved, and the mass becomes somewhat deeper in colour. When the nitrobenzene has been added, the flask is heated for a short time on the water-bath. A few drops are then poured into a test-tube of water. The dinitrobenzene should, if the reaction is complete, separate out as a hard pale yellow cake. If it is semisolid, the heating must be continued. The contents of the flask are then poured, whilst warm, into a large quantity of water. The dinitrobenzene, which separates out, is filtered at the pump and well washed with water. It is then dried. The yield is nearly theoretical. A few grams should be recrystallised from methylated spirit. The remainder may be used for the next preparation without further purification.

$$C_6H_5 . NO_2 + HNO_3 = C_6H_4(NO_2)_2 + H_2O.$$
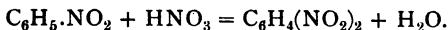
Properties.—Colourless long needles ; m.p. 89·8° ; b.p. 297°.

PREPARATION 52.

Meta-nitraniline. $C_6H_4 \begin{smallmatrix} NO_2 & 1 \\ NH_2 & 3 \end{smallmatrix}$

Hofmann, Muspratt (1846), *Ann.*, 57, 217.

    25 grms. meta-dinitrobenzene.
    75   ,,   methylated spirit.
    12   ,,   conc. ammonia.

The powdered dinitrobenzene, spirit and ammonia, are mixed together in a flask (½ litre) and weighed. Sulphuretted hydrogen, washed through water, is passed into the dark red pasty

mass, which is occasionally stirred.* The dinitrobenzene slowly dissolves, whilst at the same time crystalline flakes of ammonium thiosulphate are deposited. When the solution is saturated with the gas, the flask is removed and heated on the water-bath with an upright condenser, until the excess of sulphuretted hydrogen is expelled ($\frac{1}{4}$ hour). After cooling, the liquid is again saturated with sulphuretted hydrogen as before and then heated on the water-bath, and the process repeated until the flask has increased about 15 grams in weight. Water is now added to the liquid until nothing further is precipitated. The mixture is filtered at the pump and washed with a little water. The solid residue is transferred to a flask and shaken up with successive small quantities of warm dilute hydrochloric acid and the liquid decanted through the original filter. The nitraniline dissolves, leaving the sulphur. When no more nitraniline is extracted, (this may be ascertained by adding ammonia in excess to a portion of the acid solution, when no precipitate is formed) the acid solution is somewhat concentrated, cooled, and concentrated ammonia added. The meta-nitraniline is precipitated, filtered, and purified by recrystallisation from boiling water. The filtrate from the nitraniline may be concentrated on the water-bath and a further small quantity obtained. Yield, about 15 grams.

$$C_6H_4(NO_2)_2 + 3NH_4HS = C_6H_4NO_2.NH_2 + 3NH_3 + 3S + 2H_2O.$$

Properties.—Yellow needles; m.p. 114°; b.p. 285°. With tin and hydrochloric acid it is reduced to meta-phenylene-diamine, $C_6H_4(NH_2)_2$.

<div align="center">

PREPARATION 53.

Dimethylaniline. $C_6H_5N(CH_3)_2$

Poirrier, Chappat (1866), *Jahresb.*, 903.

</div>

20 grms. aniline hydrochloride.
15   ,,   aniline.
22   ,,   methyl alcohol.

The aniline hydrochloride is prepared by gradually adding conc. hydrochloric acid to aniline (20 grams in a beaker) until a drop brought on to a piece of filter paper, stained with

methyl violet, turns it green. The liquid is quickly cooled and stirred so as to produce small crystals. It is then filtered, well pressed, and dried on a porous plate. The dry hydrochloride is brought into a thick-walled tube closed at one end, and the mixture of aniline and methyl alcohol added. The tube is then sealed in the ordinary way and heated in the tube furnace gradually to 150° during two hours, and then to 180—200° for six hours more. The contents of the tube divide into two layers, the lower one consisting of the hydrochloride of the base and water, and the upper one of the free bases. The whole of the contents are poured out into a large separating funnel, and caustic soda added in excess. The addition of a little ether causes the bases to separate out more readily. The top layer is separated, and the lower aqueous portion is shaken up twice with small quantities of ether. The ethereal solution is dehydrated over solid caustic potash, the liquid filtered and the ether removed on the water-bath. The residue is now boiled with 25 grams acetic anhydride, using an upright condenser, for an hour in the same flask, the side limb of which is stoppered. The contents are then distilled. Unchanged acetic anhydride passes over at 130—150°; the thermometer then rises, and the portion boiling at 190—200° is collected separately. When the higher temperature is reached, it is advisable to keep only the lower half of the condenser filled with water. The distillate has a bright amber colour. Yield, 20 grams. The residue in the flask consists of acetanilide and methylacetanilide and solidifies on cooling.
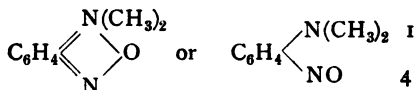
$$C_6H_5NH_2 + C_6H_5NH_2.HCl + 4CH_3OH = C_6H_5N(CH_3)_2HCl$$
$$+ C_6H_5N(CH_3)_2 + 4H_2O.$$
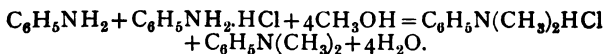
Properties.—Colourless liquid ; b.p. 192° ; sp. gr. ·9553.

Reaction.—Warm, with an equal volume of methyl iodide ; the crystalline quaternary ammonium iodide will be formed,

$$C_6H_5N(CH_3)_2 + CH_3I = C_6H_5N(CH_3)_2.CH_3I.$$
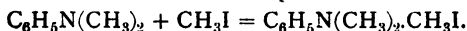
Preparation 54.

Para-nitrosodimethylaniline.

$$C_6H_4 \langle \overset{N(CH_3)_2}{\underset{N}{\diagdown O}} \quad \text{or} \quad C_6H_4 \langle \overset{N(CH_3)_2 \quad 1}{NO \quad 4}$$

Baeyer, Caro (1874), *Ber.*, 7, 810 and 963 ; Meldola (1881), *Chem. Soc. J.*, 39, 37.

    20 grms. dimethylaniline.
    52   ,,   (45 c.c.) conc. hydrochloric acid diluted with
                100 c.c. of water.
    12   ,,   · sodium nitrite (in 20 c.c. of water.)

The dimethylaniline is dissolved in the dilute hydrochloric acid in a beaker and cooled in a freezing mixture. The sodium nitrite, dissolved in a small quantity of water, is then slowly added with frequent stirring. The separation of the hydro-chloride of nitrosodimethylaniline in the form of small yellow needles soon begins, and the liquid is gradually filled with a thick crystalline deposit. When, after standing for a short time (half an hour), no further increase in the quantity of crystals is observed, the mass is filtered at the pump and washed with methylated spirit, to which one or two c.c. of concentrated hydro-chloric acid has been added. It is then washed once or twice with spirit, drained and pressed on a porous plate. Yield, nearly theoretical. It may be recrystallized by adding small quantities of hot water, until the salt is just dissolved, and then setting aside to cool. If the free base is to be prepared, recrystal-lisation is unnecessary. Ten grams of the hydrochloride are mixed into a paste with water in a flask, and caustic soda solution added in the cold until alkaline. The yellow colour of the salt changes to green of the free base. Sufficient ether is added to dissolve the green precipitate. The ethereal solution is carefully separated by means of a separating-funnel and most of the ether is then removed by distillation. The remaining

liquid is poured out into a beaker and set aside to crystallise. The base remains on evaporation of the ether in the form of brilliant green foliated crystals.

$$C_6H_5N(CH_3)_2HCl + HNO_2 = (NO)C_6H_4N(CH_3)_2.HCl + H_2O$$
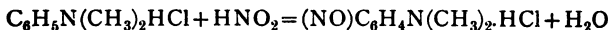
Properties.—Large green foliated crystals ; m.p. 85°.

Reactions.—1. Dissolve a few crystals in dilute hydrochloric acid and add a little zinc dust. The solution is decolourised through the formation of dimethyl *p*-phenylenediamine $(CH_3)_2N.C_6H_4NH_2$.

2. Warm a few of the crystals with ammonium sulphide solution for a few minutes, acidify with hydrochloric acid, and finally add a little ferric chloride. A deep blue colouration is produced, due to the formation of methylene blue.

3. Dissolve 6 grams of caustic soda in 250 c.c. of water and heat to boiling. Add 5 grams of the hydrochloride of nitroso-dimethylaniline gradually. The free base, which separates out in oily drops is allowed to dissolve before each fresh addition. The boiling is continued until the dark green colour of the liquid changes to reddish yellow. Dimethylamine is evolved and is easily recognized by its smell. After cooling, acidify the liquid in the flask and extract with ether. On distilling off the ether, nitrosophenol (quinoneoxime) remains in the form of dark-coloured crystals, which are difficult to purify. $C_6H_4{\overset{\textstyle N(CH_3)_2}{\underset{\textstyle NO}{\big<}}} +$

$H_2O = C_6H_4{\overset{\textstyle O}{\underset{\textstyle NOH}{\big<}}} + NH(CH_3)_2$. The presence of a nitroso-compound may be detected as follows : Melt together a minute quantity of nitrosophenol and a few crystals of phenol. Add about 2 c.c. concentrated sulphuric acid and warm very gently. A blue solution is obtained, which changes to red on dilution with water, and back to blue on adding alkali (Liebermann's "nitroso" reaction ; see Reaction, p. 155).

PREPARATION 55.

Thiocarbanilide (Diphenylthiourea) $CS\left\langle{NHC_6H_5 \atop NHC_6H_5}\right.$

Hofmann (1849), *Ann.*, 70, 142.

> 30 grms. aniline.
> 30   ,,   carbon bisulphide
> 30   ,,   absolute alcohol.

The aniline, carbon bisulphide,[1] and alcohol are poured into a round flask ($\frac{1}{2}$ litre), and heated for a day (8 hours) on the water-bath with upright condenser. As sulphuretted hydrogen is evolved, the operation must either be conducted in the fume cupboard or an exit tube must be attached to the top of the condenser tube dipping into soda-lime. The contents of the flask solidify after a time. When the reaction is complete, the condenser is reversed, and excess of carbon bisulphide and alcohol distilled off on the water-bath. The residue is washed on to a filter with very dilute hydrochloric acid, to remove any unchanged aniline, and then with water. The crystals are dried on a porous plate, and a portion crystallized from methylated spirit. Yield, 30—35 grams.

$$2C_6H_5.NH_2 + CS_2 = CS(NHC_6H_5)_2 + H_2S$$
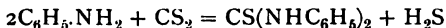
Properties.—Colourless rhombic plates ; m.p. 151° ; scarcely soluble in water, easily soluble in alcohol and ether.

PREPARATION 56.

Phenyl Thiocarbimide (Phenyl Mustard Oil) $C_6H_5N:CS$.

Hofmann (1858), *Jahresb.*, 349.

> 25 grms. thiocarbanilide
> 60 c.c. conc. hydrochloric acid.

The thiocarbanilide is boiled with two to three times the quantity of concentrated hydrochloric acid in a flask with an upright condenser for half an hour. It is decomposed into

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[1] Carbon bisulphide being very volatile and exceedingly inflammable, great care must be taken when using it in the neighbourhood of a flame.

triphenylguanidine, which remains as the hydrochloride in solution (it is subsequently separated) and phenyl mustard oil, which separates out as a brown oil. On distilling the product in steam, the phenyl mustard oil is carried over into the receiver. It is separated by shaking out with ether, and removing the ethereal layer with a tap-funnel. It is dehydrated over calcium chloride, and decanted into a small distilling flask. The ether is removed on the water-bath and the mustard oil distilled, with the thermometer, using a short condenser tube. Yield, 9—10 grams.

Properties—Colourless oil with a peculiar smell ; b.p. 220° ; sp. gr. 1·135 at 15°.

Reactions—1. Heat gently for a few minutes ·5 c.c. phenyl mustard oil, ·5 c.c. alcohol and 1½ c.c. concentrated ammonia. On cooling, thiocarbanilamide $NH_2.CS.NH.C_6H_5$ crystallises in needles.

2. Heat gently ·5 c.c. phenyl mustard oil, and ·5 c.c. aniline ; on cooling and rubbing with a glass rod, thiocarbanilide crystallises.

3. Heat on the water-bath in a small flask with upright condenser 3 grams of phenyl mustard oil and 10 c.c. absolute alcohol for 3 hours, and pour into cold water. Phenylthiourethane $C_6H_5NH.CS.OC_2H_5$, separates out and may be recrystallised from alcohol. Yield, 2½ grams ; m.p. 67°.

4. Heat a few drops of the mustard oil with yellow mercuric oxide and notice the irritating smell of phenyl isocyanate.

$$C_6H_5N{:}CS + HgO = C_6H_5N{:}CO + HgS$$
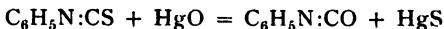
Triphenylguanidine—In order to separate the triphenylguanidine remaining in the flask as hydrochloride after distilling off the phenyl mustard oil, the hot solution must be somewhat concentrated. The colourless salt, which crystallises out on cooling, is filtered and washed with a little water. It is then warmed gently for a few minutes with dilute caustic soda solution. The base is liberated, filtered, washed with water and recrystallised from spirit.

$$2CS(NHC_6H_5)_2 + HCl = CSNC_6H_5 + C.NHC_6H_5.HCl + H_2S$$

with $.NHC_6H_5$ above and $:NC_6H_5$ below on the third term.

Thiocarbanilide.　　　Phenyl Mustard　Triphenylguanidine
　　　　　　　　　　　　　Oil.　　　　Hydrochloride.
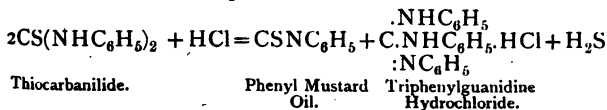
Properties—Colourless needles ; m.p. 143°.

*Reaction*—Boil for a short time with moderately strong caustic soda solution. Aniline is formed.

$$C:NC_6H_5(NHC_6H_5)_2 + 2NaOH + H_2O = 3C_6H_5NH_2 + Na_2CO_3.$$
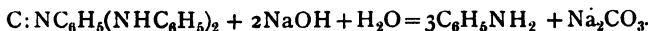
PREPARATION 57.

Diazobenzene Sulphate. $C_6H_5N:N.SO_4H.$

Griess (1866), *Ann.*, 137, 76 ; Knoevenagel (1895), *Ber.* 28, 2,049.

> 15 grms. aniline.
> 140 ,, absolute alcohol.[1]
> 30 ,, conc. sulphuric acid.
> 20 ,, amyl nitrite.

Mix the aniline and alcohol and add the concentrated sulphuric acid, in a slow stream with constant shaking. The precipitate of aniline sulphate, which first appears, redissolves. Cool the mixture to 30° and keep at 25—30° (thermometer in the liquid) whilst the amyl nitrite is dropped in from a tap-funnel. Then cool in ice water and leave for half an hour. The diazobenzene sulphate separates as a colourless micro-crystalline mass. It is filtered at the pump and washed with a little alcohol. Although diazobenzene sulphate is much more stable than the nitrate, it is undesirable to let the precipitate become quite dry. The various reactions described below are carried out with the slightly moist and well pressed precipitate.
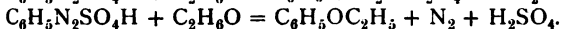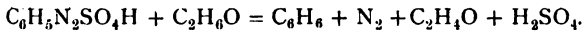
$$(C_6H_5NH_2)_2H_2SO_4 + 2C_5H_{11}ONO + H_2SO_4 = 2C_6H_5N:N.SO_4H$$
$$+ 2C_5H_{11}OH + 2H_2O.$$
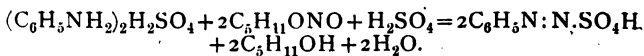
Properties.—Colourless crystals ; soluble in water and methyl alcohol ; slightly soluble in ethyl alcohol.

Reactions.—The following reactions are performed in test-tubes with about a gram of the substance.

1. Warm the substance with a few c.c. of ethyl alcohol. Vigorous effervescence occurs and the liquid turns red. When

---

[1] Neither methylated spirit nor methyl alcohol can be substituted.

effervescence ceases, add water. An oil separates out on the surface consisting of benzene mixed with a little phenetol.

$$C_6H_5N_2SO_4H + C_2H_6O = C_6H_6 + N_2 + C_2H_4O + H_2SO_4.$$
$$C_6H_5N_2SO_4H + C_2H_6O = C_6H_5OC_2H_5 + N_2 + H_2SO_4.$$

2. Dissolve the substance in a few c.c. of cold water and add a solution of bromine in potassium bromide until no further turbidity is produced. A black oil collects at the bottom of the test-tube. Pour off the top layer as far as possible, and let the oil stand in cold water. It solidifies. This is the perbromide of diazobenzene.

$$C_6H_5N_2SO_4H + KBr + Br_2 = C_6H_5NBrNBr_2 + KHSO_4.$$
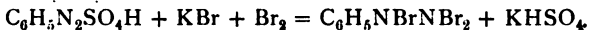
Decant any liquid and warm the perbromide with a little alcohol. Nitrogen and bromine are given off and bromobenzene is formed.

$$C_6H_5NBrNBr_2 = C_6H_5Br + N_2 + Br_2.$$
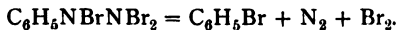
3. Dissolve the substance in a little cold water and add potassium iodide solution. Effervescence occurs and a dark coloured liquid separates out. This is iodobenzene.

$$C_6H_5N_2SO_4H + KI = C_6H_5I + N_2 + KHSO_4.$$
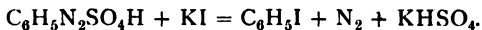
4. Dissolve the substance in water and warm gently. Effervescence occurs and a dark coloured oil separates, which has the smell of phenol. When effervescence ceases, cool and shake up with a little ether. Decant the ether into a dry test-tube. Evaporate the ether and test the residue for phenol, see p. 155

$$C_6H_5N_2SO_4H + H_2O = C_6H_5OH + H_2SO_4 + N_2.$$
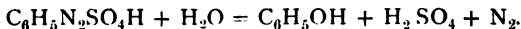
5. Dissolve the substance in cold water and add it to a solution of phenol in caustic soda, drop by drop. An orange crystalline precipitate of oxyazobenzene is formed. Repeat, using β-naphthol in place of phenol. A scarlet precipitate is obtained.

$$C_6H_5N_2SO_4H + C_6H_5ONa = C_6H_5N:N.C_6H_4ONa + Na_2SO_4$$
$$+ 2NaOH \qquad\qquad\qquad + 2H_2O$$
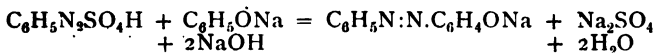
6. Dissolve in cold water and add a few drops of aniline, and shake up. Diazoamidobenzene separates out as a yellow crystalline precipitate.

$$C_6H_5N_2SO_4H + C_6H_5NH_2 = C_6H_5N:N.NHC_6H_5 + H_2SO_4.$$
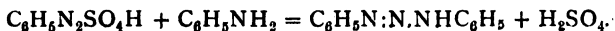
7. Heat ·5 gram of the dry substance on an iron tray. It decomposes with explosion.

Any of the diazo-compound which remains over should be dissolved in water and poured away.

PREPARATION 58.

Para-cresol, $C_6H_4 \begin{array}{c} CH_3\ 1 \\ OH\ 4 \end{array}$
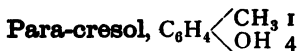
Griess (1866), *Ann.*, 137, 39 ; Ihle (1876), *J. Prakt. Ch.* 14, 451.

    25 grms. para-toluidine.
    25 ,,   conc. sulphuric acid (in 750 c.c. water).
    20 ,,   sodium nitrite (in 40 c.c. water).

Mix the dilute sulphuric acid and toluidine in a large round flask ($1\frac{1}{2}$ litre) and cool to the ordinary temperature. The nitrite solution is gradually added. The clear solution is then gently warmed on the water-bath until the evolution of nitrogen ceases. The solution, which has become very dark coloured, is distilled in steam until the distillate produces only a slight precipitate with bromine water (500 c.c.). A small quantity of tarry residue remains. The distillate is then extracted three times with small quantities (50 c.c.) of ether. The ethereal solution is dehydrated over plaster of ·Paris, filtered, and the ether removed on the water-bath. The para-cresol is then distilled over the flame with a condenser tube, and collected at 195—200°. The distillate, which has a yellow colour, solidifies on cooling. Yield 10—15 grams.

$$(CH_3.C_6H_4NH_2)_2\ H_2SO_4 + 2NaNO_2 = 2CH_3.C_6H_4.OH$$
$$+ 2N_2 + Na_2SO_4 + 2H_2O.$$
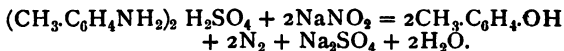
Properties.—Colourless crystals ; m. p. 36° ; b. p. 198°.

Reactions.—Make a solution of para-cresol by shaking up a few drops with 5 c.c. of water. To one portion add a few drops of bromine water. A white precipitate of tetrabromocresol is formed. To another portion add a drop of ferric chloride. A blue colouration is produced.
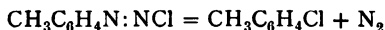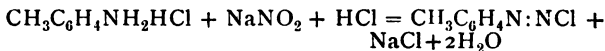
PREPARATION 59.

Para-chlorotoluene, $C_6H_4\begin{smallmatrix}CH_3 & 1\\ Cl & 4\end{smallmatrix}$

Sandmeyer (1884), *Ber.*, 17, 2651 ; Wynne (1892), *Chem. Soc. J.*, 61, 1072.

    50 grms. para-toluidine.
   120 c.c.   conc. hydrochloric acid (in 80 c.c water).
    40 grms. sodium nitrite (in 100 c.c. water).
    30   ,,   copper carbonate to be dissolved in 300 c.c.
              conc. hydrochloric acid.

Dissolve the para-toluidine in the hydrochloric acid and then cool quickly in a beaker, and stir so as to obtain small crystals. Place the beaker in ice and, whilst it is cooling down to 0°, prepare a solution of cuprous chloride. Dissolve the copper carbonate in the hydrochloric acid, and boil with excess of copper turnings until a nearly colourless solution is obtained. The solution is decanted into a large round flask (2 litres) and placed in ice, and 50 grams of ice thrown into the liquid. Whilst this solution is cooling to 0° the diazotoluene chloride is prepared by adding the sodium nitrite solution gradually to the para-toluidine hydrochloride and stirring. The temperature should not rise above 10°. When three-quarters of the nitrite has been added, test occasionally with potassium iodide-starch paper until a drop gives an immediate deep blue or dark brown colouration. Add this solution gradually in portions of about 20 c.c. at a time to the cold solution of the cuprous chloride, and shake up well after each addition. Towards the end, throw in a few lumps of ice. A thick crystalline mass of orange coloured needles, consisting, probably of the diazo-copper salt separates, and, on standing, decomposes slowly, forming a dark coloured liquid. After standing over night, the liquid is distilled in steam. The distillate is shaken up with a little caustic soda to remove cresol, and the chlorotoluene, which sinks to the bottom, is separated. The liquid is further shaken out with a little ether, and the ethereal solution added to the chlorotoluene, and the whole dehydrated with calcium chloride. The liquid is decanted, the ether distilled

off on the water-bath and the residue collected at 155—165°. Yield, about 45 grams.

$$CH_3C_6H_4NH_2HCl + NaNO_2 + HCl = CH_3C_6H_4N:NCl + NaCl + 2H_2O$$

$$CH_3C_6H_4N:NCl = CH_3C_6H_4Cl + N_2$$

Properties.—Colourless liquid ; b. p. 162° ; m. p. 7·4°.

PREPARATION 60.

Para-iodotoluene.

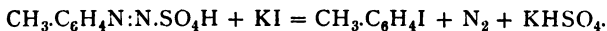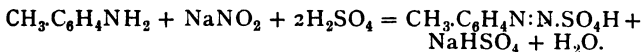Griess (1866), *Ann.*, 137, 76.

25 grms. para-toluidine.
50 „   conc. sulphuric acid (in 250 c.c. water).
20 „   sodium nitrite (in 40 c.c. water).
60 „   potassium iodide (in 100 c.c. water).

Mix the dilute sulphuric acid and para-toluidine in a large beaker (1½ litre) and cool to 0° in a freezing mixture. Stir, whilst cooling, to produce small crystals of the sulphate. Add the solution of sodium nitrite slowly, and if the temperature rises above 10°, add a few lumps of ice. When three quarters of the nitrite solution has been added, test occasionally with potassium iodide-starch paper until a blue or brown stain is produced. Now add the solution of potassium iodide gradually, and, after well stirring, leave the mixture at the ordinary temperature for an hour, and then warm cautiously on the water-bath until effervescence ceases. The liquid is dark coloured, and a black oil settles to the bottom of the vessel, which when cold solidifies. The oil consists of iodotoluene, and the dark colour of the solution is due to free iodine, which may be removed by the addition of a gram or two of sodium bisulphite. The mixture is now distilled in steam, using a beaker as receiver. Care must be taken to prevent the condenser tube becoming blocked by the iodotoluene, which is solid at the ordinary temperature. This is effected by running the water very slowly through the condenser so that the upper part remains warm. The iodotoluene solidifies

in the receiver. It has a yellow tint, which may be removed by recrystallisation from methylated spirit. Yield, 45—50 grams.

$$CH_3.C_6H_4NH_2 + NaNO_2 + 2H_2SO_4 = CH_3.C_6H_4N:N.SO_4H + NaHSO_4 + H_2O.$$

$$CH_3.C_6H_4N:N.SO_4H + KI = CH_3.C_6H_4I + N_2 + KHSO_4.$$

Properties.—Colourless plates ; m. p. 35° ; b. p. 211—212°.

Reactions.—1. *Iodobenzoic Acid.*—Boil 10 grms. iodotoluene with 12 grms. permanganate dissolved in 300 c.c. of water in a brine or calcium chloride bath, with upright condenser, for a day. The bath should keep the contents of the flask boiling briskly. The oily drops of iodotoluene will gradually cease to drip from the condenser, and the permanganate will be nearly de-colourised.

The precipitated manganese dioxide is now dissolved as sul-phate by passing in sulphur dioxide gas until the last trace of brown precipitate has disappeared. The colourless iodobenzoic acid comes down in the acid solution on cooling, and is filtered and recrystallised from spirit ; m. p. 265°. The yield is theoretical.

$$CH_3.C_6H_4I + O_3 = COOH.C_6H_4I + H_2O.$$

2. *Tolyliodochloride.*—Dissolve 10 grams iodotoluene in five times its weight of chloroform, cool in ice, and pass in dry chlorine until saturated. Chlorine is conveniently made by dropping concentrated hydrochloric acid from a tap-funnel on to powdered potassium bichromate in a round flask, heated on the water-bath. The chlorine is dried through concentrated sul-phuric acid. When chlorine is no longer absorbed, the yellow needle-shaped crystals of the iodochloride are filtered, washed with a little chloroform, and dried on a porous plate.

$$CH_3.C_6H_4I + Cl_2 = CH_3.C_6H_4ICl_2.$$
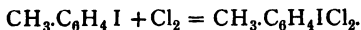
3. *Iodosotoluene.*—Dissolve 2·5 grams caustic soda in 20 c.c. water, and grind with 5 grams of iodochloride in a mortar. Leave over night and then filter and wash with water. The colourless crystals of the iodoso-compound are dried on a porous plate.

$$CH_3.C_6H_4ICl_2 + 2NaOH = CH_3.C_6H_4IO + 2NaCl + H_2O.$$

COHEN'S ADV. P. O. C.

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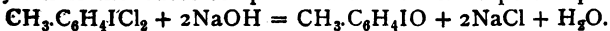
PREPARATION 61.

Para-tolylcyanide. $C_6H_4\left<{CH_3\ 1\atop CN\ \ 4}\right.$.

Sandmeyer (1884), *Ber.*, 17, 2653.
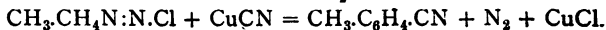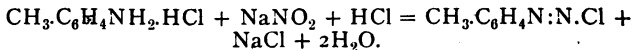
</div>

20 grms. para-toluidine.

45 c.c. conc. hydrochloric acid (in 150 c.c. water)

16 grms. sodium nitrite (in 40 c.c. water).

50   „   copper sulphate (in 200 c.c. water).

55   „   potassium cyanide (in 100 c.c. water).

The copper sulphate is dissolved in 200 c.c. water on the water-bath in a round flask (2 litres). The potassium cyanide is gradually added to the warm solution.* The cuprous cyanide dissolves in excess of the potassium cyanide and cyanogen gas is liberated. $2CuSO_4 + 4KCN = 2CuCN + 2K_2SO_4 + (CN)_2$. The solution is left, whilst the para-toluidine is diazotised. The base is dissolved in the dilute hydrochloric acid, cooled in ice, and well stirred. The mixture is kept cold whilst the sodium nitrite solution is gradually added, until it gives an immediate colouration with potassium iodide-starch paper. The diazo-solution is then added in portions of about 10 c.c. at a time to the warm cuprous cyanide solution, with frequent shaking. A rapid effervescence occurs, nitrogen and some hydrocyanic acid being evolved. When, in the course of about fifteen minutes, the diazo-solution has been added, it is left on the water-bath until effervescence ceases ($\frac{1}{4}$ hour). The liquid turns a dark colour, and a black tarry deposit is formed. The product is distilled in steam. This should be carried out in the fume cupboard, as not only is hydrocyanic acid liberated, but a small quantity of isocyanide which is formed in the reaction, produces an intolerable smell. The distillation is continued until no more yellow oil passes over. The tolyl cyanide solidifies in the receiver on cooling, as a yellow crystal-line mass which is filtered, dried on a porous plate, and may be purified by distillation ; but for the preparation of toluic acid this is unnecessary. Yield, about 15 grams.

$$CH_3.C_6H_4NH_2.HCl + NaNO_2 + HCl = CH_3.C_6H_4N:N.Cl + NaCl + 2H_2O.$$

$$CH_3.CH_4N:N.Cl + CuCN = CH_3.C_6H_4.CN + N_2 + CuCl.$$

Properties.—Colourless crystals ; m.p. 38° ; b.p. 218°.

Reaction.—Para-toluic acid. Boil up 10 grms. tolylcyanide with 60 c.c. conc. sulphuric acid and 20 c.c. water, in a round flask with upright condenser until colourless crystals of toluic acid appear in the condenser tube (about half an hour). On cooling, the acid crystallises out, and is separated by filtration, washed with water and recrystallised from hot water ; m. p. 177°.

$$CH_3.C_6H_4.CN + 2H_2O + H_2SO_4 = CH_3.C_6H_4.CO.OH$$
$$+ NH_4.H.SO_4.$$
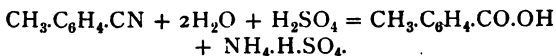
The yield is nearly theoretical.

PREPARATION 62.

Diazoamidobenzene. $C_6H_5N:N.NH.C_6H_5.$

Griess (1866), *Ann.*, 137, 58 ; Staedel, Bauer (1886), *Ber.*, 19, 1952.

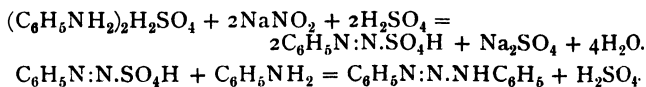>   20 grms. aniline.
>   6   ,,   conc. sulphuric acid.
>   600   ,,   water.
>   7·4 ,,   sodium nitrite.

The acid is poured into the water contained in a large beaker (1 litre) and the aniline then added. About half the aniline dissolves as sulphate. The liquid is warmed in the water-bath to 27° and the sodium nitrite dissolved in a small quantity of water is slowly added, and the whole well stirred. The temperature is maintained at 27—30° for a quarter of an hour. As soon as the sodium nitrite is added the liquid turns yellow and rapidly becomes turbid from the formation of diazoamidobenzene, which separates out in yellowish brown crystalline crusts. The solution is now allowed to stand at the ordinary temperature for half an hour, when nearly the whole of the diazoamido-benzene crystallises out. It is filtered, washed with cold water, pressed well on the filter, and dried on a porous plate or a pad of filter paper. It forms a brown sandy powder and may be purified by recrystallisation from benzene or alcohol. In crystallising, it is necessary to bring the substance into solution as quickly as possible. Boiling spirit (about three times the weight of substance) should be added and the liquid heated for

L 2

a moment until a clear solution is obtained and then allowed to cool. On prolonged boiling it decomposes. For the preparation of amidoazobenzene the dry powder is sufficiently pure. Yield, nearly theoretical.

$$(C_6H_5NH_2)_2H_2SO_4 + 2NaNO_2 + 2H_2SO_4 =$$
$$2C_6H_5N:N.SO_4H + Na_2SO_4 + 4H_2O.$$
$$C_6H_5N:N.SO_4H + C_6H_5NH_2 = C_6H_5N:N.NHC_6H_5 + H_2SO_4.$$

N.B.—The sulphuric acid, set free in the second phase of the reaction, acts upon the sodium nitrite, so that one molecule only is required.

Properties.—Golden yellow plates (from alcohol) m.p. 91°; insoluble in water; it explodes when heated above its melting point.

Reaction.—Dissolve a little of the substance in alcohol and add a drop or two of an alcoholic solution of silver nitrate. A red crystalline precipitate of $C_6H_5N:N.NAg.C_6H_5$ is deposited.

PREPARATION 63.

Amidoazobenzene (Aniline yellow). $C_6H_5N:NC_6H_4NH_2$.

Mène (1861), *Jahresb.*, 496 ; Kekulé (1866), *Zeitsch. f. Ch.*, 2, 689 ; Staedel, Bauer (1886), *Ber.*, 19, 1953.

> 10 grms. diazoamidobenzene.
> 25   „   aniline.
> 5   „   aniline hydrochloride.

The finely powdered diazoamidobenzene, aniline hydrochloride (see p. 134) and aniline are mixed together and heated to 40° for an hour. The mixture forms a clear deep red solution. After standing for 24 hours at the ordinary temperature, the diazoamidobenzene is converted into amidoazobenzene. A slight excess of moderately strong hydrochloric acid is added, care being taken that no great evolution of heat occurs. On cooling, the amidoazobenzene separates out together with aniline hydrochloride. It is filtered and washed with cold, very dilute hydrochloric acid, when small violet crystals of amidoazobenzene hydrochloride remain on the filter. In order to obtain the free base, the hydrochloride is warmed with dilute ammonia. The base, which has a brown colour, is filtered and dissolved in

hot methylated spirit and with the addition of a few drops of concentrated ammonia.   Yield, about 8 grams.

$$C_6H_5N:N.NHC_6H_5 + H.C_6H_4NH_2.HCl =$$
$$C_6H_5N:N.C_6H_4NH_2 + C_6H_5NH_2.HCl.$$
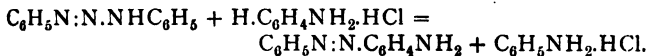
Properties.—Orange prisms ; m.p. 127°.

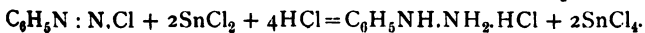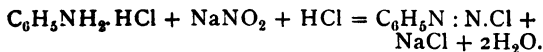### PREPARATION 64.

Phenylhydrazine. $C_6H_5NH.NH_2$.

E. Fischer (1878), *Ann.*, 190, 167 ; Meyer, Lecco (1883), *Ber.*, 16, 2976 ; Meyer and Jacobson, *Lehrbuch.* 2, 305.

20 grms.	aniline.
200 ,,	(170 c.c.) conc. hydrochloric acid.
20 ,,	sodium nitrite (in 100 c.c. water).
120 ,,	crystallised stannous chloride (in 100 c.c. conc. hydrochloric acid).

The aniline is dissolved in the concentrated hydrochloric acid and cooled to 0° in a freezing mixture.   The solution of sodium nitrite is gradually added, the temperature being kept at 0°, until a drop of the mixture, diluted with water, turns potassium iodide-starch paper blue.   To the mixture, still cooled in ice, 100 grams stannous chloride, dissolved in about an equal weight of conc. hydrochloric acid, is added.   A thick white crystalline precipitate of phenylhydrazine hydrochloride separates.   It is allowed to stand for half an hour and filtered at the pump ; it is then separated as far as possible from the mother liquor, and transferred to a flask.   The free base is obtained by decomposing the hydrochloride with caustic soda.   An excess of caustic soda is added, and the mixture well shaken.   The free base, which separates as a reddish-coloured oil, is extracted with ether, and the ethereal solution dehydrated over solid potassium carbonate.   The ether is then removed on the water-bath, and the residual oil either used without further purification or distilled *in vacuo*.   Yield, 15—20 grams.

$$C_6H_5NH_2.HCl + NaNO_2 + HCl = C_6H_5N:N.Cl +$$
$$NaCl + 2H_2O.$$
$$C_6H_5N:N.Cl + 2SnCl_2 + 4HCl = C_6H_5NH.NH_2.HCl + 2SnCl_4.$$

Properties.—Nearly colourless oil when freshly distilled; b. p. 241—242°; m. p. 17·5°; sp. gr. 1·097 at 23°.

Reactions.—1. Add a few drops of phenylhydrazine to 2 c.c. of water, then a drop or two of copper sulphate solution and excess of caustic soda. Cuprous oxide is precipitated with effervescence and benzene separates, $C_6H_5NH.NH_2 + 2CuO = C_6H_6 + N_2 + Cu_2O + H_2O$. The same reaction takes place if the phenylhydrazine is dissolved in dilute acetic acid and copper sulphate solution added and warmed.

2. Add to a few drops of phenylhydrazine an equal quantity of glacial acetic acid, dilute with a little water, and add a drop of benzaldehyde. In a short time the phenylhydrazone of benzaldehyde will crystallise out.

See also the Reactions on pp. 110 and 120.

PREPARATION 65.

Sulphanilic Acid. $C_6H : \begin{matrix} NH_2 & 1 \\ SO_3H & 4 \end{matrix}$
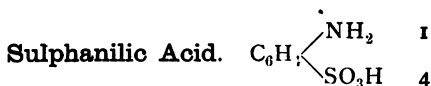
Gerhardt (1846), *Ann.*, 60, 312 ; Buckton, Hofmann (1856) *Ann.*, 100, 163.

> 25 grms. aniline.
> 80   ,,   conc. sulphuric acid.

The aniline and sulphuric acid are cautiously mixed in a round flask (250 c.c.) and heated to 180—190° in an oil or metal bath for four to five hours until a sample dissolved in water remains clear on the addition of caustic soda in excess and no aniline separates. The product is poured into cold water, which precipitates the sulphanilic acid as a grey crystalline mass. It is filtered, washed with a little cold water, recrystallised from hot water with the addition of a little animal charcoal, and dried in the air. Yield, 25—30 grams.
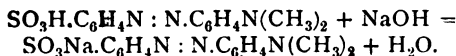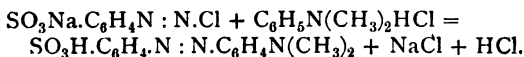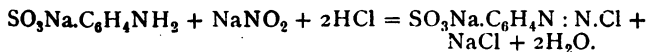
$$C_6H_5NH_2 + H_2SO_4 = NH_2.C_6H_4.SO_3H + H_2O.$$

Properties.—Colourless rhombic plates, containing 2 mols. of water of crystallisation, which they lose slowly in the air, and the crystals fall to powder.

PREPARATION 66.

Methyl Orange (Helianthin). $SO_3Na.C_6H_4N : N.C_6H_4N(CH_3)_2$

  10 grms. sulphanilic acid.[1]

  2·5 ,,   anhydrous sodium carbonate (in 100 c.c. water).

  3·5 ,,   sodium nitrite (in 20 c.c. water).

  6   ,,   conc. hydrochloric acid (in 10 c.c. water).

  6   ,,   dimethylaniline (in 6 c.c. conc. HCl and 20 c.c. water).

The sulphanilic acid is dissolved in the sodium carbonate ($\frac{1}{2}$ mol.) solution and the sodium nitrite (1 mol.) solution added. The mixture is cooled in ice, and the solution of hydrochloric acid (1 mol.) gradually added. The solution of dimethylaniline (1 mol.) is now poured in, and the liquid made alkaline with caustic soda. The separation of methyl orange at once begins, and is assisted by the addition of a little common salt (20 grams). The precipitate is filtered at the pump, and crystallised from hot water.   Yield, nearly theoretical.

$$SO_3Na.C_6H_4NH_2 + NaNO_2 + 2HCl = SO_3Na.C_6H_4N : N.Cl + NaCl + 2H_2O.$$

$$SO_3Na.C_6H_4N : N.Cl + C_6H_5N(CH_3)_2HCl =$$
$$SO_3H.C_6H_4.N : N.C_6H_4N(CH_3)_2 + NaCl + HCl.$$

$$SO_3H.C_6H_4N : N.C_6H_4N(CH_3)_2 + NaOH =$$
$$SO_3Na.C_6H_4N : N.C_6H_4N(CH_3)_2 + H_2O.$$

Properties.—Methyl orange is the sodium salt of the sulphonic acid, and dissolves in water with a yellow colour.   The free acid is red, and its action as an indicator depends upon this change on the addition of mineral acid.   It is decomposed, like the majority of azo-compounds, by stannous chloride in hydrochloric acid into two molecules, produced by the addition of hydrogen to the double-linked nitrogen atoms.
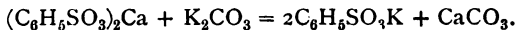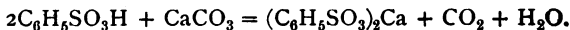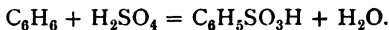
$$HSO_3.C_6H_4N : N.C_6H_4N(CH_3)_2 + 2SnCl_2 + 4HCl =$$
$$HSO_3.C_6H_4NH_2 + H_2NC_6H_4N(CH_3)_2 + 2SnCl_4.$$

PREPARATION 67.

Potassium Benzene Sulphonate. $C_6H_5.SO_3K + \frac{1}{2}H_2O.$

Mitscherlich (1834), *Pogg. Ann.*, 31, 283 and 364; Michael, Adair (1877), *Ber.*, 10, 585.

> 50 grms. benzene.
> 100   ,,   conc. sulphuric acid.

The benzene and sulphuric acid are heated together on a sand-bath in a round flask ($\frac{1}{2}$ litre) with upright condenser. The mixture is kept at a gentle boil until the top layer of benzene has been nearly absorbed by the sulphuric acid (six to eight hours). On cooling, the dark coloured liquid is poured into cold water (1 litre) contained in a large basin, boiled up and neutralised with powdered chalk or thick milk of lime. The mass is filtered hot through a porcelain funnel or cloth from the precipitate of calcium sulphate, washed with hot water and somewhat concentrated. The solution, which contains the calcium salt of benzene sulphonic acid, is treated with just sufficient potassium carbonate solution to precipitate the calcium as carbonate and convert the sulphonic acid into the potassium salt. This is ascertained by filtering small samples and testing the filtrate with potassium carbonate. The liquid is again filtered through cloth or through a porcelain funnel and concentrated first over a ring burner, and finally on the water-bath, until a sample crystallises on cooling. The potassium salt is drained at the pump and dried on a porous plate. Yield, about 80 grams.

$$C_6H_6 + H_2SO_4 = C_6H_5SO_3H + H_2O.$$

$$2C_6H_5SO_3H + CaCO_3 = (C_6H_5SO_3)_2Ca + CO_2 + H_2O.$$

$$(C_6H_5SO_3)_2Ca + K_2CO_3 = 2C_6H_5SO_3K + CaCO_3.$$

Properties.—Colourless, pearly plates, which slowly effloresce in the air and which melt above 300° with slight decomposition; very soluble in water.

PREPARATION 68.

Benzenesulphonic Chloride. $C_6H_5SO_2Cl$.

Gerhardt, Chiozza (1853), *Ann.*, 87, 299.

15 grms. potassium benzene sulphonate.
25   „   phosphorus pentachloride.

The potassium benzene sulphonate is carefully dried on the water-bath, powdered and mixed with the phosphorus penta-chloride in a flask.* A vigorous reaction occurs. When it has abated, the flask is heated on the water-bath for one hour,* and the mass occasionally stirred with a glass rod. The pro-duct is poured into a flask containing 200 c.c. cold water and allowed to stand an hour. The sulphonic chloride, which separates as an oil, is then extracted with ether, dehydrated over calcium chloride, decanted, and the ether removed on the water-bath. Yield, 10 grams of a light brown oil.

$$C_6H_5SO_3K + PCl_5 = C_6H_5SO_2Cl + POCl_3 + KCl.$$

Properties.—Colourless oil when pure ; b. p. 246—247° with decomposition ; distils undecomposed *in vacuo.*

Reaction.—1. Grind up in a mortar 1 c.c. of sulphonic chloride with 5 grams powdered ammonium carbonate, and leave on the water-bath until the smell of the sulphonic chloride has gone. Add water, filter, and wash and crystallise the residue of benzene sulphonamide from spirit, $C_6H_5SO_2Cl + 2NH_4HCO_3 = C_6H_5SO_2NH_2 + 2H_2O + 2CO_2 + NH_4Cl.$

2. Add 1 c.c. of the sulphonic chloride to 2 c.c. aniline, stir up well, add water, and acidify with a few drops of concentrated HCl (methyl violet paper). Filter, wash, and crystallise the benzenesulphonanilide from spirit, $C_6H_3SO_2Cl + NH_2C_6H_5 = C_6H_5SO_2NHC_6H_5 + HCl.$

3. Add 2 c.c. absolute alcohol to 1 cc. sulphonic chloride and excess of caustic soda until alkaline ; warm gently for five minutes and add more caustic soda if necessary. Cool, and extract with ether. The residual liquid consists of benzene ethyl sulphonate, $C_6H_5SO_2Cl + HOC_2H_5 = C_6H_5SO_2OC_2H_5 + HCl.$

4. Repeat 3, using phenol in place of alcohol.

<center>PREPARATION 69.</center>

Phenol.   (Carbolic Acid, Hydroxybenzene), $C_6H_5.OH$.

Kekulé, Wurtz, Dusart (1867), *Zeitschr. f. Ch. N. F.*, 3, 299–301 ; Degener (1878), *Journ. prakt. Ch.* (2), 17, 394.

> 20 grms. potassium benzene sulphonate.
> 35 „   caustic potash.

The caustic potash is dissolved in the smallest quantity of water (5 c.c.) by heating in a silver or nickel basin or crucible, and the powdered potassium benzene sulphonate added. The temperature of the melt, which during the process is kept constantly stirred, must not exceed 250°. It is convenient to use the thermometer as stirrer, the bulb and part of the stem being encased in a glass tube closed at one end. When the requisite temperature has been reached, a small flame is sufficient to maintain it. The mass is first thick and pasty, but soon becomes semi-fluid and remains in this condition, gradually changing in colour from yellow to brown. Towards the end of the operation (one hour) it regains somewhat its original consistency. On cooling, the melt is dissolved in a little water, and the alkaline reddish-brown liquid (potassium phenate and excess of alkali) acidified with concentrated hydrochloric acid in the cold. Phenol separates out as a light yellow oil, which is extracted three times with ether. The ethereal solution dehydrated over potassium carbonate is distilled, first on the water-bath until the ether is removed, and then over the flame. The portion boiling at 175—185° is nearly pure phenol. It distils as a colourless liquid and solidifies at once on cooling. Yield, 6—7 grams.

$$C_6H_5SO_3K + KOH = C_6H_5OK + KHSO_3.$$
$$C_6H_5OK + HCl = C_6H_5OH + KCl.$$
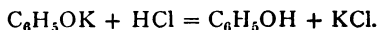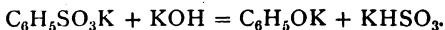
Properties.—Colourless needles, with a characteristic smell ; m. p. 42–-43° ; b. p. 182° ; easily soluble in alcohol and ether, and in about 15 parts of water at the ordinary temperature ; produces blisters on the skin.

Reactions.—1. Make a solution of phenol in water, and to one portion add a drop of ferric chloride. A violet colouration is produced.

2. Add to another portion a drop of bromine water. A white crystalline precipitate of tribromophenol is formed.

3. To a third portion add an equal volume of dilute ammonia and a few drops of sodium hypochlorite and warm gently. A copper-sulphate-blue colour is produced.

4. Add a small fragment of solid sodium nitrite to 5 c.c. concentrated sulphuric and warm very gently until dissolved. On adding about ·5 gram of phenol, a brown solution is obtained, which rapidly changes to deep blue. If the blue solution is poured into water, a cherry red colouration is produced, which changes to blue on the addition of an alkali (Liebermann's 'nitroso' reaction, see p. 137).
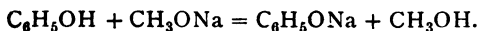
PREPARATION 70.

Anisol. (Methyl Phenate, Phenyl Methyl Ether), $C_6H_5.O.CH_3$.

Cahours (1851), *Ann.*, 78, 226.

    5 grms. sodium.
  100 c.c.   methyl alcohol.
   20 grms. phenol.
   40   ,,   methyl iodide.

The methyl alcohol is poured into a round flask (250 c.c.) connected with an upright condenser. The sodium, cut into small pieces, is then added, the flask being detached from the condenser for a moment and replaced. When the sodium has dissolved, the phenol and methyl iodide are added. The mixture is heated on the water-bath until the solution has no longer an alkaline reaction (two to three hours). As much as possible of the methyl alcohol is distilled off on the water-bath and water added to the amber-coloured residue. A colourless oil separates out, which is extracted with ether. The ethereal solution is dehydrated over calcium chloride and distilled, first on the water-bath until the ether has been driven off, and then over

the flame. Almost the whole of the residue distils at 150—155°.
Yield, nearly theoretical.

$$C_6H_5OH + CH_3ONa = C_6H_5ONa + CH_3OH.$$
$$C_6H_5ONa + CH_3I = C_6H_5OCH_3 + NaI.$$
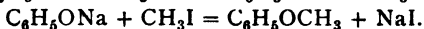
Properties.—Colourless liquid, possessing an agreeable smell ;
b. p. 152° ; sp. gr. ·991 at 15°.

PREPARATION 71.

Ortho- and Para-nitrophenol. $C_6H_4 \begin{smallmatrix} OH & 1 & 1 \\ NO_2 & 2 & 4 \end{smallmatrix}$.

Hofmann (1857), *Ann.,* 103, 347 ; Fritsche (1859), *Ann.,* 110,
150 ; Kekulé, *Lehrbuch d. org. chem.,* 3, 40.

    40 grms. phenol.
    70   ,,   (50 c.c.) conc. nitric acid (in 170 c.c. water).

The phenol, melted in a basin on the water-bath, is slowly
added in small quantities to the nitric acid and water contained
in a large round flask (1 litre), and the contents of the flask
well shaken.   On the addition of the phenol, the liquid immedi-
ately changes to a deep brown or black colour, and a heavy,
dark-brown oil separates out.   When the phenol has been
added, the mixture is allowed to stand for 12 hours.   The oil
has by that time collected at the bottom of the vessel, and may
be freed from acid by repeatedly decanting and pouring in
fresh water (three or four times).   The contents of the flask
consist of nearly equal quantities of para- and ortho-nitrophenol,
mixed with resinous products.   In order to separate the two
isomers, the product is distilled in a current of steam (see Fig.
63, p. 94) until the distillate is almost colourless.   The ortho-
compound distils in the form of a yellow oil, which may solidify
in the condenser, in which event the water is temporarily run
out of the condenser.   The solid in the receiver is separated by
filtration and dissolved in spirit at 40°, to which water is then
added, drop by drop, until a turbidity is produced.   Yield, 15
grams.   The solid residue contains the para-compound mixed
with black, resinous substances, from which it is separated by
repeatedly extracting with boiling water.   The united portions
of the aqueous extract are boiled with animal charcoal for
half an hour in a large basin, and filtered through a fluted filter

moistened with water. The filtrate is made alkaline with caustic soda solution, and concentrated to a small bulk (100 c.c.). If tarry matter separates, it must be filtered through a wet filter. To obtain the free para-compound, the concentrated aqueous solution of the sodium salt is cooled, and the separated sodium salt filtered. The crystals are dissolved and acidified with concentrated hydrochloric acid, and the nitrophenol, which separates, is filtered and recrystallised from hot water. Yield, 10 grams.

$$C_6H_5OH + HONO_2 = OHC_6H_4NO_2 + H_2O.$$
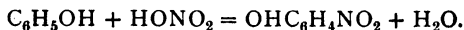
Properties.—Ortho-nitrophenol, sulphur-yellow needles, possessing a peculiar smell ; m. p. $45°$; b. p. $214°$; distillable with steam ; soluble in alcohol, ether, and hot water ; less soluble in cold water.

Para-nitrophenol, colourless needles ; m.p. $114°$; easily soluble in alcohol and hot water ; slightly soluble in cold water.

PREPARATION 72.

Picric Acid (Trinitrophenol). $C_6H_2(OH){<}\begin{matrix}NO_2 & 2 \\ NO_2 & 4. \\ NO_2 & 6\end{matrix}$
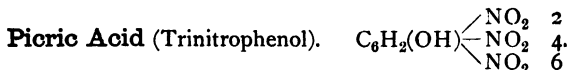
Woulfe (1771) ; Schmidt, Glutz (1869), *Ber.*, 2, 52.
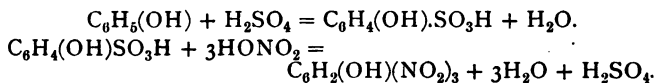
25 grms. phenol.
25   „   conc. sulphuric acid.
100   „   (70 c.c.) conc. nitric acid, sp. gr. 1·4.
25   „   (20 c.c.) fuming nitric acid, sp. gr. 1·5.

The phenol and concentrated sulphuric acid are heated together in a porcelain basin for a few minutes, until a clear solution of phenol sulphonic acid is obtained. It is diluted with half its volume of water, well cooled, and then slowly added, in small quantities at a time, from a tap-funnel, to the nitric acid contained in a flask (1 litre), and well shaken.* The liquid assumes a deep red colour, a considerable rise of temperature occurs, and red fumes are evolved. When the phenol sulphonic acid has been added, the flask is placed on the water-bath and heated, with the addition of 25 grams fuming nitric acid, for 1—2 hours.* On cooling, picric acid separates

out as a yellow, crystalline mass. It is diluted with water, filtered at the pump, and washed free from the mother liquor with cold water. It is then purified by recrystallisation from a large quantity of hot water acidified with a few drops of sulphuric acid. Yield, about 30 grams.

$$C_6H_5(OH) + H_2SO_4 = C_6H_4(OH).SO_3H + H_2O.$$
$$C_6H_4(OH)SO_3H + 3HONO_2 =$$
$$C_6H_2(OH)(NO_2)_3 + 3H_2O + H_2SO_4.$$

Properties.—Yellow, prismatic crystals ; m. p. 122·5° ; sublimes on gently heating ; explodes on detonation ; easily soluble in alcohol and ether ; with difficulty in cold, more readily in hot water ; the solution has a bitter taste.

Reactions.—1. To an aqueous solution of picric acid add a little potassium cyanide solution, and warm. A brown crystalline precipitate of isopurpuric acid separates.

2. Add picric acid and a few drops of caustic soda to a dilute solution of grape sugar, and warm. The liquid turns deep brown.

3. Dissolve naphthalene in a little spirit, and add an equal quantity of a solution of picric acid in spirit. On cooling, yellow needles of naphthalene picrate separate, $C_{10}H_8.C_6H_2OH(NO_2)_3$. Benzene forms colourless crystals, anthracene, scarlet needles, having a similar composition.

PREPARATION 73.

Phenolphthalein. $C\begin{cases}(C_6H_4OH)_2 \\ C_6H_4CO.O\end{cases}$
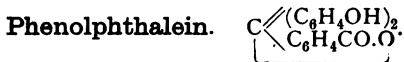
Baeyer (1876), *Ber.*, 9, 1230, and (1880), *Ann.*, 202, 68.

   10 grms. phthalic anhydride.
        20   „   phenol.
         8   „   conc. sulphuric acid.

The phthalic anhydride, phenol, and concentrated sulphuric acid are heated together to 115 – 120° in the oil-bath 8—9 hours. The mass becomes semi-fluid and of a dark red colour. It is poured, whilst hot, into a basin of water (500 c.c.) and boiled until the smell of phenol has disappeared, the water being renewed as it evaporates. The undissolved yellow granular

precipitate, on cooling, is separated from the liquid by filtration, and washed with water. It is then dissolved in dilute caustic soda solution, filtered from the undissolved residue, and the filtrate acidified with acetic acid and a few drops of hydrochloric acid. The phthalein separates out, after standing for some hours, as a light yellow, sandy powder, which is filtered and dried. It is purified by dissolving in absolute alcohol with the addition of animal charcoal (1 part phenolphthalein, 6 parts alcohol, and $\frac{1}{2}$ part charcoal) and boiling the solution on the water-bath for an hour. The mass is filtered hot, washed with two parts boiling alcohol and the filtrate evaporated down to two-thirds its bulk on the water-bath. On adding 8 times the quantity of cold water to the cooled solution, the latter becomes turbid. The liquid is well stirred, and, after standing a few seconds, filtered through cloth from the resinous oil which separates. On heating the filtrate on the water-bath to expel excess of alcohol, phenolphthalein crystallises out in the form of a white powder. Yield, 5 grams.

$$2C_6H_5(OH) + C_6H_4{<}^{CO}_{CO}{>}O = C_6H_4{<}^{C(C_6H_4OH)_2}_{CO}{>}O + H_2O.$$
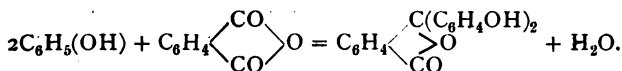
Properties.—White, granular, crystalline powder; m. p. 250—253°; very slightly soluble in water, readily soluble in hot alcohol; soluble in alkalis with a crimson colour.

PREPARATION 74.

Salicylaldehyde (ortho-oxybenzaldehyde)
#### Para-oxybenzaldehyde.

Reimer, Tiemann (1876), *Ber.*, 9, 824.

$$C_6H_4{<}^{OH\quad 1\quad 1}_{CO.H\quad 2\quad 4}.$$

50	grms.	phenol.
100	,,	caustic soda.
160	,,	water.
75	,,	chloroform.

The phenol, caustic soda and water are mixed together in a round flask (1 litre) with an upright condenser attached and heated to 50—60°. The chloroform is then added gradually

through the top of the condenser and, after each addition, the flask is well shaken. A gentle reaction sets in, and the temperature rises. At the same time the surface of the brownish yellow solution takes a violet tint, which rapidly fades, the liquid finally assuming a deep red colour. When all the chloroform has been added, the contents of the flask are boiled for half an hour. A yellow semi-solid mass separates out of the solution. The unattacked chloroform is now distilled off on the waterbath, the liquid diluted with water and strongly acidified with dilute hydrochloric or sulphuric acid. A thick red oil separates out on the surface and is subjected to distillation in steam. An oil, having a faintly yellow colour, distils over with the water, and settles to the bottom of the receiver. When drops of oil cease to condense, the distillation is stopped. The distillate, which contains salicylaldehyde and phenol, is extracted with ether, and the ethereal solution well shaken with a saturated solution of sodium bisulphite (see Reaction 2, p. 60). The bisulphite compound of salicylaldehyde separates out in colourless needles, which are filtered, washed free from traces of phenol with alcohol and then decomposed by heating with dilute sulphuric acid. The aldehyde which separates is taken up with ether, dehydrated over calcium chloride, the ether driven off and the aldehyde distilled. Yield, 10 grams. In the distilling flask from which the salicylaldehyde has in the first instance been removed with steam, there remains a brownish liquid and a dark red substance, which sinks to the bottom of the vessel, and forms a brittle resin on cooling. The aqueous portion is filtered hot through a moistened filter, which retains the resin, and the filtrate, containing para-oxybenzaldehyde, is extracted when cold with ether. On distilling off the solvent, the aldehyde remains in the form of a yellow mass of stellar-shaped needles, which may be purified by crystallisation from hot water. Yield, about 2 grams.

$$C_6H_5ONa + 3NaOH + CHCl_3 = C_6H_4{<}^{ONa}_{CO.H} +$$
$$3NaCl + 2H_2O.$$
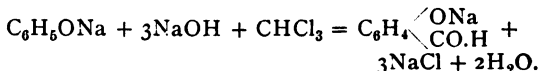
Properties.—Salicylaldehyde. Colourless fragrant oil, b. p. 196·5; sp. gr. 1·173 at 13·5°; solidifies at 20°, forming large crystals. Volatile in steam; soluble in water; miscible in all proportions with alcohol and ether.

Reaction.—Add a drop of ferric chloride to the aqueous solution of the aldehyde. A deep violet colouration is produced.

Para-oxybenzaldehyde.—Colourless needles, m. p. 115—116°; scarcely soluble in cold water, readily in hot water, alcohol and ether. Non-volatile in steam. The bisulphite of sodium compound dissolves readily in water.

Reaction.—The same as above; but the colouration is less intense.

PREPARATION 75.

Salicylic Acid (Ortho-oxybenzoic Acid). $C_6H_4 \begin{matrix} OH \\ CO.OH \end{matrix}$

Kolbe, *J. prakt. Chem.* (2), 10, 95.

10 grms. caustic soda.
23 „ phenol.

This preparation should be commenced first thing in the morning. Dissolve the caustic soda in about 10 c.c. of water in a small porcelain basin and add the phenol. Heat the basin on wire-gauze over a very small flame, and, whilst holding it firmly with a small clamp (tongs are too insecure), keep constantly stirring with a glass rod. After a short time the mass becomes stiff and balls together. The basin should now be removed from the gauze, and the mass stirred and broken up as it cools. When still warm, it is sufficiently hard to powder in a mortar. It is quickly powdered and transferred to a small retort (200 c.c.) heated in an oil or paraffin bath to 130—140°, and exhausted by attaching it to a receiver and water-jet aspirator as shown in Fig. 62, p. 92, but without thermometer. In about an hour all the moisture is removed, and the body of the retort appears dry. The aspirator is stopped, and the receiver detached. The light coloured mass in the retort is broken up and shaken into a mortar, when it is quickly powdered and replaced. The object of the above series of operations is to obtain perfectly dry, uncharred and well-powdered sodium phenate, upon which the success of the preparation entirely depends. A moderate stream of carbon dioxide, dried through concentrated sulphuric acid is

COHEN'S ADV. P. O. C. M

now passed over the surface of the sodium phenate by means of a bent tube fixed through the tubulus of the retort, and terminating just above the substance. The temperature of the oil-bath is gradually raised from 140° to 180—190°, whilst fresh surfaces are exposed by occasionally stirring with a glass rod inserted for a moment through the tubulus. At the end of four hours the temperature is raised to 190—200° for another hour, and the process stopped. During the heating a considerable quantity of phenol distils, and solidifies in the neck of the retort, whilst the contents become dark coloured. The mass is shaken out into a basin without disturbing the phenol in the neck, and the residue dissolved by filling the retort two-thirds full of water. This is poured into the basin containing the other portion, which soon dissolves. The solution is acidified with concentrated hydrochloric acid, which throws down impure salicylic acid in the form of a dark brown precipitate. When cold, the precipitate is filtered at the pump, and washed with a little cold water. A further quantity may be obtained by evaporating the filtrate to a small bulk. It is purified by dissolving in boiling water and filtering. The filtrate deposits the acid, on cooling, in needles which have a faint brown colour. Yield about 6 grams.

1. $C_6H_5ONa + CO_2 = C_6H_5O.CO.ONa$
   Sodium phenyl carbonate.
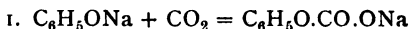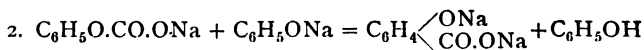
2. $C_6H_5O.CO.ONa + C_6H_5ONa = C_6H_4{\displaystyle {ONa \atop CO.ONa}} + C_6H_5OH$
   Disodium salicylate.

Properties.—Colourless needles; m. p. 155—156°; soluble in alcohol and hot water. 100 parts water dissolve ·225 parts at 15° and 7·925 parts at 100°.

Reactions.—1. Dissolve a little of the acid in water and add a drop of ferric chloride. A violet colouration is obtained.

2. Grind up some of the acid with soda-lime and cover with a shallow layer of the same substance. On heating strongly the smell of phenol is perceived.

$$C_6H_4(OH)CO.OH + CaO = C_6H_5OH + CaCO_3.$$
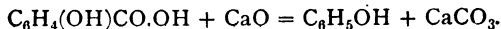
PREPARATION 76.

Quinone and Quinol (Hydroquinone).

$$C_6H_4{<\!\!<}^{O}_{O} \text{ and } C_6H_4{<}^{OH\ 1}_{OH\ 4}$$
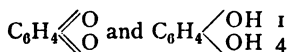
Woskresensky (1838), *Ann.*, 27, 268; Nietzki (1886), *Ber.*, 19, 1467; Meyer and Jacobson, *Lehrbuch*, vol. ii., 421.

> 25 grms. aniline.
> 200   „   (110 c.c.) conc. sulphuric acid.
> 750 c.c. water.
> 80 grms. potassium bichromate[1].

The water and aniline are mixed together in a large glass jar (1½ litres) and the sulphuric acid added. The mixture is cooled in ice and stirred with a turbine (see Fig. 59, p. 83). The finely-powdered bichromate is added every few minutes in small quantities on the end of a small spatula, until about one-third has been added, care being taken that the temperature does not exceed 10°. The mixture is then left to stand over night, and the remaining two-thirds of the bichromate introduced as before. Aniline black separates out in the first part of the operation, and in the second part of the process gradually dissolves, giving a deep brown solution. The liquid, after standing for four to five hours more, is divided into two about equal portions. One half is shaken up, not too vigorously, with a large quantity (200 c.c.) of ether three times. The same ether may be distilled and used again. Vigorous shaking produces an emulsion, which very slowly separates. On distilling off the ether, the quinone remains in the form of yellow needle-shaped crystals, which may be purified by sublimation. The substance is placed in a flask attached to a condenser, and a rapid current of steam blown through. The quinone sublimes and collects in the receiver, and is separated from the water by filtration, and dried. Yield about 10 grams.

The reaction consists in the oxidation and elimination of the amido-

---

[1] Or an equivalent quantity of sodium bichromate (75 grams), which may be dissolved in 3—4 times its weight of water and delivered from a tap-funnel.

group and simultaneous replacement of two hydrogen atoms in the benzene nucleus by oxygen, and cannot well be expressed in the form of equation (see Appendix, p. 246).

Properties. — Golden-yellow, needle-shaped crystals ; m.p. 116° ; with difficulty soluble in water, readily soluble in alcohol and ether ; sublimes on heating ; its vapour has a penetrating smell and attacks the eyes.

Reaction.—Dissolve a few crystals in water and add a solution of sulphur dioxide. The solution first darkens from the formation of quinhydrone, $C_6H_4.O_2.C_6H_4(OH)_2$, and then becomes colourless and contains quinol.

Quinol.—The other half of the product is treated with a current of sulphur dioxide until, after standing for a time, it retains the smell of the gas.* The sulphur dioxide is most conveniently obtained from a bottle of liquid, or it may be prepared by dropping concentrated sulphuric acid from a tap-funnel on to sodium sulphite. The liquid, after standing one to two hours, is extracted with ether until no more quinol is removed. The ether is distilled off, and the dark coloured residue recrystallised from water with the addition of sulphur dioxide and a little animal charcoal. Yield about 10 grams.

$$C_6H_4O_2 + SO_2 + 2H_2O = C_6H_4(OH)_2 + H_2SO_4.$$
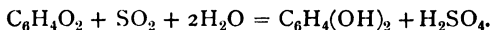
Properties.—Colourless prisms ; m. p. 169° ; sublimes at a gentle heat ; easily soluble in alcohol, ether, and hot water.

Reactions.—1. To a solution of quinol in water, add a few drops of ferric chloride. The solution turns brown and ether now extracts quinone.

$$C_6H_4(OH)_2 + 2FeCl_3 = C_6H_4O_2 + 2FeCl_2 + 2HCl.$$
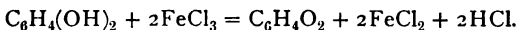
2. Add to the solution of quinol in water, a drop of copper sulphate, and caustic soda, and warm. Cuprous oxide is precipitated.

$$C_6H_4(OH)_2 + 2CuO = C_6H_4O_2 + Cu_2O + H_2O.$$
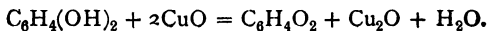
PREPARATION 77.

Benzyl Chloride. $C_6H_5CH_2Cl$.

Cannizzaro (1853), *Ann.*, 88, 129.

100 grms. toluene.

The apparatus consists of vessels for evolving and drying chlo-
rine (see Fig. 57, p. 80) and a weighed retort (300 c.c.) standing
on wire-gauze, into which the toluene is brought. (Fig. 77.) The
chlorine enters through an inlet tube, fixed through the tubulus
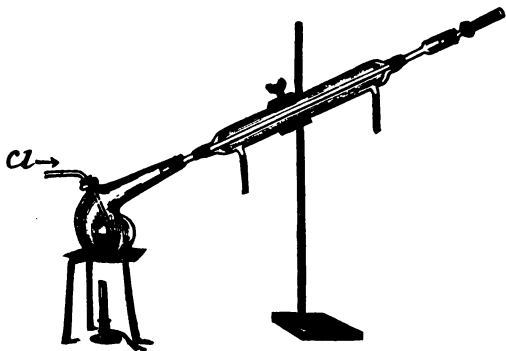of the retort, the neck being fixed to an upright condenser. The

FIG. 77.

dry chlorine is conducted into the toluene, which is kept boiling
gently until it has gained about 37 grams in weight.* The liquid
turns yellow, and hydrochloric acid fumes are evolved at the
upper end of the condenser.   When the reaction is complete the
contents of the retort are distilled.*   At first unchanged toluene
distils; the fraction boiling at $165°—185°$ contains nearly the
whole of the benzyl chloride, and forms the greater part of
the product.   The liquid which passes over above $185°$ is a
mixture of higher chlorinated compounds, and consists chiefly
of benzal chloride, $C_6H_5CHCl_2$, and benzotrichloride, $C_6H_5CCl_3$.

The portion containing the benzyl chloride is repeatedly fractionated until a liquid is obtained, boiling at 176°—180°, which is nearly pure benzyl chloride.   Yield 80—90 grams.

$$C_6H_5CH_3 + Cl_2 = C_6H_5CH_2Ci + HCl.$$
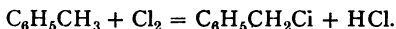
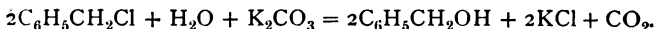*Properties.*—Colourless liquid with an irritating smell; b. p. 179°; sp. gr. 1·107 at 14°.

Preparation 78.

Benzyl Alcohol. $C_6H_5CH_2OH.$

Söderbaum, Widman (1892), *Ber.*, 25, 3290.

20 grms. benzyl chloride.
16   „   potassium carbonate (in 200 c.c. water).

In a round flask ($\frac{1}{2}$ litre) attached to an upright condenser, boil the mixture of benzyl chloride and potassium carbonate solution over wire-gauze with the addition of a few bits of porous pot.   The boiling must be continued until the smell of benzyl chloride has disappeared (6—8 hours).   Extract the liquid with ether, dehydrate over potassium carbonate, decant through a filter and distil off the ether on the water-bath.   Continue the distillation over wire-gauze, run the water out of the condenser and collect at 200°—210°.   Yield 12—15 grams.

$$2C_6H_5CH_2Cl + H_2O + K_2CO_3 = 2C_6H_5CH_2OH + 2KCl + CO_2.$$

Properties.— Colourless liquid with a faint aromatic smell; b. p. 206·5°; sp. gr. 1·05 at 15·4°; moderately soluble in water.

Reactions.— 1. Boil 2 or 3 drops with 2—3 c.c. dilute nitric acid ($1HNO_3:4H_2O$); benzaldehyde is first formed and is detected by the smell.   On continued boiling, benzoic acid is formed and separates on cooling in crystals.

2. Warm 1 c.c. of the alcohol with 1 c.c. concentrated hydrochloric acid.   The clear solution becomes turbid and benzyl chloride separates out.

$$C_6H_5CH_2OH + HCl = C_6H_5CH_2Cl + H_2O.$$
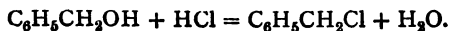
PREPARATION 79.

Benzaldehyde (Bitter Almond Oil). $C_6H_5.CO.H.$

Liebig, Wöhler (1837), *Ann.*, 22, 1 ; Lauth, Grimaux (1867), *Ann.*, 143, 186.

> 50 grms. benzyl chloride.
> 40   „   copper nitrate.
> 500   „   water.

The mixture of benzyl chloride, copper nitrate and water are heated to boiling in a round flask (1½ litres) with upright condenser on the sand-bath for a day (8—9 hours).   A slow current of carbon dioxide is at the same time passed through the liquid to prevent oxidation of the benzaldehyde by absorption of oxygen from the air.   During the process nitrous fumes are slowly evolved.   When the reaction is complete, the contents of the flask are extracted with ether, and the yellow oil remaining, after distilling off the ether, is well shaken with a saturated solution of sodium bisulphite [1] and allowed to stand for a time.   The colourless crystalline mass which separates out is filtered, washed with a little alcohol and ether, and then drained in a porcelain filter.   The aldehyde is regained by adding dilute sulphuric acid in excess and distilling in steam. The distillate is extracted with ether, dehydrated over calcium chloride, decanted, and the ether distilled off.   Yield, about 15 grams.

$$2C_6H_5CH_2Cl + Cu(NO_3)_2 = 2C_6H_5COH + CuCl_2 + 2HNO_2.$$
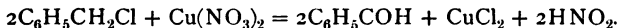
Properties.—Colourless liquid, with a pleasant smell ; b. p. 179° ; sp. gr. 1·0504 at 15° ; it quickly oxidises in the air, forming benzoic acid.

Reactions.—1. Leave a drop of benzaldehyde on a watch glass.   It solidifies by becoming oxidised to benzoic acid.

2. Add 5 c.c. concentrated ammonia to 1 c.c. benzaldehyde, cork up and leave two days.   Crystals of hydrobenzamide

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[1] The solution is prepared either by dissolving solid sodium bisulphite in water or by passing sulphur dioxide into powdered sodium carbonate covered with a layer of water.   The carbonate dissolves with effervescence, forming a heavy apple-green liquid smelling strongly of sulphur dioxide.

$(C_6H_5CH)_3N_2$ separate out, which may be recrystallised from spirit.

$$3C_6H_5COH + 2NH_3 = (C_6H_5CH)_3N_2 + 3H_2O.$$
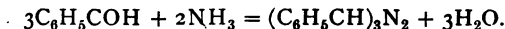
3. Heat on the water-bath 2 c.c. benzaldehyde and 2 c.c. aniline for an hour. Crystals of benzalaniline are formed on cooling, $C_6H_5COH + C_6H_5NH_2 = C_6H_5CH:N.C_6H_5 + H_2O$, which may be filtered and crystallised from spirit ; m. p. 42°.

4. Shake up together 10 grams of benzaldehyde with 9 grams caustic potash in 6 c.c. of water until a permanent emulsion is formed and let stand 3—4 hours. Dissolve the solid product in a little water and shake out with ether twice. On acidifying the aqueous portion with hydrochloric acid, benzoic acid is precipitated. Filter and wash with a little cold water and dry. Distil the ether from the ethereal solution. The residue is benzyl alcohol. $2C_6H_5COH + KOH = C_6H_5COOK + C_6H_5CH_2OH.$ (Cannizzaro).

See also Reactions on p. 60 and p. 150.

See also Reactions on p. 60 and p. 150.

PREPARATION 80.
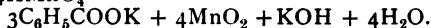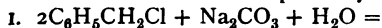
Benzoic Acid. $C_6H_5CO.OH_3$.

5 grms. benzyl chloride.
4 „ anhydrous sodium carbonate (in 50 c.c. water).
8·5 „ potassium permanganate (in 150 c.c. water).

The benzyl chloride and sodium carbonate solution are mixed in a round flask ($\frac{1}{2}$ litre) attached to an upright condenser, and boiled gently over wire-gauze, whilst the permanganate solution is gradually dropped in from a tap-funnel pushed through the top of the condenser. In the course of 2—3 hours the pink colour of the permanganate will have vanished and been replaced by a mass of dark brown precipitate of manganese dioxide. When the liquid is cold, a stream of sulphur dioxide is passed in until the manganese dioxide is dissolved (see p. 145). The liquid is allowed to cool and the benzoic acid, which separates, is filtered at the pump, washed with a little cold water and

recrystallised from hot water; m.p. 121°. The yield is theoretical. The reaction probably occurs in two steps.

1. $2C_6H_5CH_2Cl + Na_2CO_3 + H_2O =$

$$2C_6H_5CH_2OH + 2NaCl + CO_2.$$

2. $3C_6H_5CH_2OH + 4KMnO_4 =$
$$3C_6H_5COOK + 4MnO_2 + KOH + 4H_2O.$$

Properties.—Crystallises in needles; m. p. 121°; on heating it melts and sublimes; soluble in hot water, alcohol and ether. It distils in steam.

Reactions.—1. Make a neutral solution of ammonium benzoate by adding excess of ammonia to benzoic acid and boiling until neutral. To different portions add solutions of calcium chloride, ferric chloride, silver nitrate and lead acetate.

2. Grind up ·5 gram of the acid with four times the weight of soda-lime and heat gently at first and then more strongly. Vapours of benzene will be given off, which may be detected by the smell. $C_6H_5CO.OH + CaO = C_6H_6 + CaCO_3.$

PREPARATION 81.

Benzoin. $\begin{array}{l} C_6H_5.CHOH \\ C_6H_5.CO \end{array}$
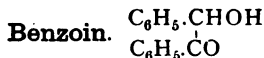
Liebig, Wöhler (1832), *Ann.*, 3, 276; Zinin (1840), *Ann.*, 34, 186.

> 25 grms. benzaldehyde.
> 5 ,, potassium cyanide (in 20 c.c. water).
> 50 c.c. absolute alcohol.

The mixture of benzaldehyde, potassium cyanide and alcohol is heated on the water-bath with an upright condenser for about half an hour. On cooling the liquid, the benzoin separates out as a mass of small colourless crystals, which are filtered and washed with a little alcohol. Yield, about 20 grams. A portion of the substance may be purified by recrystallisation from spirit.

$$2C_6H_5COH = C_6H_5CO.CH(OH).C_6H_5.$$
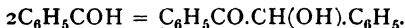
Properties. —Colourless prisms; m. p. 137°; slightly soluble in water; soluble in alcohol and ether.

Reaction.—Add Fehling's solution to benzoin dissolved · in alcohol.   Benzil is formed and cuprous oxide precipitated. Benzil is also formed on oxidation with nitric acid.

Benzil. $C_6H_5CO.CO.C_6H_5.$

15 grms. benzoin.
35 „   conc. nitric acid, sp. gr. 1·4.

The benzoin and nitric acid are heated on the water-bath with an air condenser, the flask being occasionally shaken.   Nitrous fumes are evolved, and the crystals of benzoin are converted into a yellow oil, which, after two hours' heating, is free from unchanged benzoin.   The contents of the flask are now poured into water, and the yellow crystalline deposit separated by filtration, washed with water, and recrystallised from alcohol. Yield, 10—12 grams.

Properties.—Yellow prisms ; m. p. 95° ; insoluble in water ; soluble in hot alcohol.

Reaction.—1. Dissolve a small quantity of benzil in a little alcohol, add a fragment of caustic potash and boil.   A violet solution is obtained.


Benzilic Acid. $(C_6H_5)_2C(OH).CO_2H.$

10 grms. benzil.
50   „   caustic potash.

The caustic potash is melted with a small quantity of water in a silver crucible.   The temperature of the mass is brought to 150°, and the finely powdered benzil added.   The benzil melts, and the mixture shortly changes to a solid mass of potassium benzilate.   The cooled melt is dissolved in water, and the alkaline solution acidified with hydrochloric acid, which precipitates the benzilic acid.   The crystalline mass, which contains small quantities of benzoic acid, is separated from the mother-liquor and washed with cold water.   It is then transferred to a porcelain basin, dissolved in hot water, and the solution boiled

until the smell of benzoic acid has gone.   On cooling, benzilic acid crystallises out, and is purified by a second crystallisation from hot water.
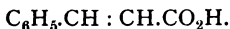
$$C_6H_5.CO.CO.C_6H_5 + KOH = (C_6H_5)_2C.(OH).COOK.$$
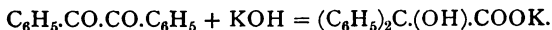
Properties.—Colourless needles ; m. p. 150° ; scarcely soluble in cold, readily in hot water and alcohol.

Reaction.—Add a little concentrated sulphuric acid to benzilic acid.   It dissolves with an intense red colour.
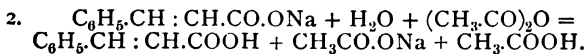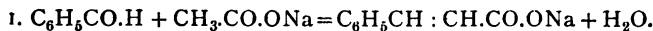
PREPARATION 82.

Cinnamic Acid (Phenylacrylic Acid).
$$C_6H_5.CH : CH.CO_2H.$$

Bertagnini (1856), *Ann.*, 100, 126 ; Perkin (1868), *Chem. Soc. J.*, 21, 53 ; Fittig (1881), *Ber.*, 14, 1826.

              20 grms. benzaldehyde.
              10   ,,   sodium acetate (fused).
              30   ,,   acetic anhydride.

The mixture of benzaldehyde, sodium acetate, and acetic anhydride is heated to 180° in a small round flask with upright condenser in an oil-bath for about eight hours.   The mass is poured out whilst hot into a large round flask (1 litre), sodium carbonate added until alkaline, and any unchanged benzaldehyde distilled off with steam.   After filtering from undissolved resinous by-products, hydrochloric acid is added, which precipitates the free cinnamic acid in white crystalline flakes, which may be purified by recrystallisation from hot water.   Yield, 15—20 grams.

1. $C_6H_5CO.H + CH_3.CO.ONa = C_6H_5CH : CH.CO.ONa + H_2O.$

2. $\quad C_6H_5.CH : CH.CO.ONa + H_2O + (CH_3.CO)_2O =$
   $C_6H_5.CH : CH.COOH + CH_3CO.ONa + CH_3.COOH.$

Properties.—Colourless prisms ; m. p. 133° ; b. p. 300—304°.

<div align="center">

PREPARATION 83.

Hydrocinnamic Acid (Phenylpropionic Acid).
$C_6H_5CH_2.CH_2.CO_2H.$
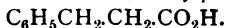
Erlenmeyer, Alexejeff (1862), *Ann.*, 121, 375, and (1866),
137, 237.

</div>

10 grms. cinnamic acid.
100   ,,   water.
170   ,,   sodium amalgam (2½ per cent.).

The sodium amalgam is prepared by warming 200 grams of mercury in a porcelain basin for a few minutes. The mercury is poured out into a mortar which is placed in the fume cupboard, the window of which is drawn down so as to protect the face. Five grams of sodium are introduced in small pieces, the size of a pea, and pressed with a pestle under the surface of the mercury. Each piece dissolves with a bright flash. The amalgam is poured out whilst semi-fluid on to an iron tray, broken up, and kept in a wide-necked stoppered bottle.[1]

The cinnamic acid and water are introduced into a strong beaker or bottle (300 c.c.), and the liquid made slightly alkaline with caustic soda, which dissolves the acid forming the sodium salt. The sodium amalgam is added in small pieces from time to time and the liquid thoroughly agitated. The solution, which remains clear, becomes slightly warm, and the amalgam soon liquefies, but no hydrogen is evolved until towards the end of the operation. When the whole of the amalgam has been added, and bubbles of gas cease to be given off, the solution is decanted from the mercury, which is rinsed with water. On acidifying the solution with hydrochloric acid, hydrocinnamic acid is precipitated as a colourless oil, which solidifies on standing. It may be recrystallised from a large quantity of warm water. Yield, 8—9 grams.

$$C_6H_5.CH : CH.CO_2H + H_2 = C_6H_5.CH_2.CH_2.CO_2H.$$
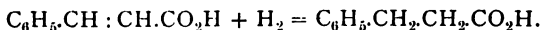
Properties.—Long colourless needles ; m. p. 47° ; b. p. 280° ; soluble in water and alcohol ; volatile in steam.

[1] If larger quantities of amalgam are required, the mercury is heated in a small enamelled pan, or crucible, the sodium added in one lot, and the vessel immediately closed with a lid, which is held down with long crucible tongs until the reaction is over, and then poured out whilst fluid.

PREPARATION 84.

Meta-bromobenzoic Acid $C_6H_4\begin{smallmatrix}Br\\CO.OH\end{smallmatrix}$ $\begin{smallmatrix}1\\3\end{smallmatrix}$

Hübner, Petermann (1869), *Ann.*, 149, 131.

> 5 grms. benzoic acid.
> 7   „   bromine.
> 30 c.c.   water.

The mixture is brought into a thick-walled tube, closed at one end and sealed in the usual way. The tube is heated in the tube furnace to 140—150°, for eight to nine hours. After cooling, the capillary is opened and the tube removed from the furnace. The bromine will have completely disappeared, and colourless crystals of bromobenzoic acid now fill the tube. The contents are removed, filtered, and boiled with water (100 c.c.) in a basin to drive off unchanged benzoic acid. The liquid is cooled, filtered, and the bromobenzoic acid crystallised from hot water. Yield, 5 grams.

$$C_6H_5CO.OH + Br_2 = C_6H_4Br.CO.OH + HBr.$$

Properties.—Colourless needles ; m. p. 183°.

PREPARATION 85.

Benzoyl Chloride. $C_6H_5CO.Cl.$

Wöhler (1832), *Ann.*, 3, 262 ; Cahours (1846), *Ann.*, 60, 255.

> 28 grms. benzoic acid.
> 50   „   phosphorus pentachloride.

A round flask (250 c.c.) is fitted with an air-condenser. The phosphorus pentachloride is introduced from the bottle and weighed by difference. The operation must be conducted in the fume-cupboard. The benzoic acid is then added, and the air-condenser attached to the flask.* The action begins almost immediately, and clouds of hydrochloric fumes are evolved. The whole contents become liquid and consist of benzoyl chloride (b. p. 200°), phosphorus oxychloride (b. p. 107°), and unchanged pentachloride. Most of the oxychloride may be removed by distilling *in vacuo* on the water-bath. The re-

mainder is fractionated at the ordinary pressure and collected at 190—200°. Yield, 20—25 grams.

$$C_6H_5COOH + PCl_5 = C_6H_5CO.Cl + POCl_3 + HCl.$$

Properties.—Colourless liquid, which fumes in the air and possesses a pungent smell ; b. p. 198·5° ; sp. gr. 1·214 at 19°.

Reactions.—1. Add a few drops of benzoyl chloride to 1 c.c. of water ; the benzoyl chloride does not decompose, and requires warming for some time before it is completely dissolved (compare acetyl chloride, p. 67).

2. Add 2 c.c. ethyl alcohol to 1 c.c. benzoyl chloride and caustic soda solution until alkaline, and warm gently. After a time the smell of benzoyl chloride disappears, and ethyl benzoate remains as an oily liquid with a fragrant smell. $C_6H_5COCl + C_2H_5OH + NaOH = C_6H_5COOC_2H_5 + NaCl + H_2O.$

3. Add 5 grams benzoyl chloride to 10 grams ammonium carbonate in a mortar * and grind up well. The reaction proceeds quietly. If after ten minutes the smell of benzoyl chloride still remains, add a few drops of concentrated ammonia. Add cold water and filter. Benzamide remains on the filter in the form of a white crystalline powder, and may be recrystallised from hot water ; m.p. 128°. $C_6H_5COCl + 2NH_4HCO_3 = C_6H_5CONH_2 + NH_4Cl + 2CO_2 + 2H_2O.$

PREPARATION 8c.

Ethyl Benzoate (Ethyl Benzoic Ester). $C_6H_5CO.OC_2H_5.$

E. Fischer and Speier, *Ber.* (1895), 28, 1150.

25 grms. benzoic acid.
75　,,　(90 c.c.) absolute alcohol.

Pass dry hydrochloric acid gas (see p. 84) through the alcohol, cooled in water until it has increased about 3 grams in weight Add the benzoic acid and boil the mixture with upright condenser over wire-gauze for two hours. On pouring a small quantity of the product into water, only the ester, which is a heavy oil, should separate, but no solid benzoic acid. The excess of alcohol is now distilled off on the water-bath and the residue poured into water. Any free hydrochloric or benzoic acid is removed by shaking with a dilute solution of sodium carbonate. On adding ether and shaking, the ester dissolves in

the top layer of ether, which is separated and dehydrated over calcium chloride. The ether is removed on the water-bath, and the ethyl benzoate is then distilled over wire-gauze, a few bits of porcelain being added to prevent bumping. The distillate is collected between 205—212°. Yield, about 22 grams.

$$C_6H_5COOH + HOC_2H_5 = C_6H_5COOC_2H_5 + H_2O.$$
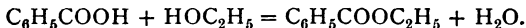
Properties.—Colourless, sweet-smelling oil; b. p. 211°; sp. gr. 1.05 at 16°.

PREPARATION 87.

Acetophenone (Phenylmethylketone, Hypnone).
$$C_6H_5.CO.CH_3.$$
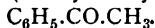
Friedel, Crafts (1884), *Ann. Ch. Phys.*, 1, 507; 14, 455.

> 30 grms. benzene.
> 50 „ aluminium chloride (anhydrous).
> 35 „ acetyl chloride.

The various reactions, known as Friedel and Crafts' reactions, are effected by means of anhydrous aluminium chloride. The aluminium chloride, being very hygroscopic, cannot be kept long, even in a stoppered bottle, without undergoing gradual decomposition. As the success of the reaction depends entirely on the quality of the chloride, it should be either freshly procured from a reliable firm or resublimed from a retort. It may also be prepared on a small scale by passing dry hydrochloric acid over heated aluminium foil or filings, but the operation is troublesome and scarcely repays the time spent. Attach a round flask (500 c.c.) to an upright condenser, and bring into it the aluminium chloride, which should be well powdered, and immediately cover it with the benzene. Place the flask in ice water, and add the acetyl chloride drop by drop from a tap-funnel, which is pushed into the top of the condenser.* A vigorous effervescence occurs, and hydrochloric acid is evolved. The contents of the flask are converted into a brown viscid mass which, after standing an hour, is stirred up and shaken into a beaker containing ice and water (250 c.c.). The mass decomposes with evolution of heat, and a dark oil separates on the surface. The liquid is poured into a separating-funnel and a little benzene added. The aqueous portion is drawn off, and

the benzene layer shaken up with dilute caustic soda and then with water. The benzene solution is finally separated, dehydrated over calcium chloride, filtered, and distilled. The benzene first passes over. The thermometer then rises quickly to 195°. The receiver is now changed, the water run out of the condenser, and the distillate, which boils at 195—200°, collected separately. It forms a pale yellow oil with a characteristic sweet smell, and solidifies completely on standing. Yield, 20—25 grams.
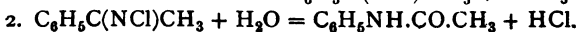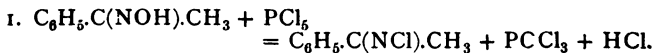
$$C_6H_6 + CH_3COCl = C_6H_5.CO.CH_3 + HCl.$$
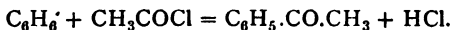
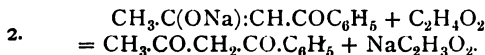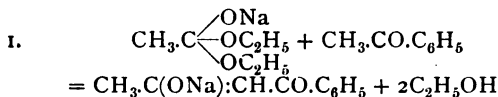*Properties.*—Colourless plates ; m. p. 20° ; b. p. 202° ; insoluble in water.

Reactions—1. *Acetophenoneoxime.* Mix together 5 grams of hydroxylamine hydrochloride dissolved in 10 c.c. of water, 8 grams of acetophenone, and 3 grams of caustic soda dissolved in a very little water. Add methylated spirit until, on warming, the solution is clear, and boil on the water-bath 2—3 hours. Pour into 100 c.c. water, and extract with ether. Distil off the ether and crystallise the solid residue from petroleum spirit. Yield, 8 grams ; m. p. 58—60°. $C_6H_5.CO.CH_3 + NH_2OH.HCl + NaOH$ $= C_6H_5C(NOH).CH_3 + NaCl + 2H_2O.$

2. *Acetophenonesemicarbazone.* Mix 1 gram of semicarbazide hydrochloride with 1·5 gram of crystallised sodium acetate, and dissolve in the smallest quantity of warm water. Add 1 gram of acetophenone and sufficient spirit to produce a clear solution when hot. Continue to heat for a few minutes. On cooling, the semicarbazone deposits as a yellow, crystalline mass. $C_6H_5.CO.CH_3 + NH_2.NH.CO.NH_2.HCl + NaC_2H_3O_2$ $= C_6H_5C(N.NH.CONH_2)CH_3 + NaCl + C_2H_4O_2.$ Theoretical yield ; m. p. 185—188°.

3. *Beckmann's Reaction.* Dissolve 1 gram of acetophenoneoxime in 30 c.c. anhydrous ether, and add gradually 1·5 gram of powdered phosphorus pentachloride. Distil off the ether, and add a little water to the residue. On cooling, crystals of acetanilide separate. Recrystallise from water, and determine the melting point.

1. $C_6H_5.C(NOH).CH_3 + PCl_5$
$= C_6H_5.C(NCl).CH_3 + PCCl_3 + HCl.$
2. $C_6H_5C(NCl)CH_3 + H_2O = C_6H_5NH.CO.CH_3 + HCl.$

4. *Benzoylacetone.* Six grams of dry, powdered, sodium ethylate are added to 20 grams of dry ethyl acetate, and cooled in water. The sodium ethylate is prepared by dissolving 4 grams of sodium in 40 c.c. absolute alcohol, and distilling off the excess of alcohol, first from the water-bath, and then from the metal-bath, in a current of dry hydrogen, the temperature of the bath being raised gradually to 200°, until nothing more passes over. The white cake is detached, rapidly powdered up, and the requisite quantity quickly weighed out and added to the ethyl acetate. After standing a quarter of an hour, 10 grams of acetophenone are added, when sodium benzoyl acetone begins to separate. A little ether is added, and after standing for a few hours the sodium compound is filtered and washed with ether. The sodium compound is then dried in the air, dissolved in cold water, and acidified with acetic acid. Benzoylacetone separates out. Yield, 9—10 grams ; m. p. 60—61°. It behaves towards ferric chloride and copper acetate like ethyl acetoacetate (see Reactions, p. 76). (Claisen.)

1.
$$CH_3.C{<}^{ONa}_{OC_2H_5}{\,}^{OC_2H_5} + CH_3.CO.C_6H_5$$
$$= CH_3.C(ONa){:}CH.CO.C_6H_5 + 2C_2H_5OH$$

2.
$$CH_3.C(ONa){:}CH.COC_6H_5 + C_2H_4O_2$$
$$= CH_3.CO.CH_2.CO.C_6H_5 + NaC_2H_3O_2.$$

PREPARATION 88.

Diphenylmethane. $C_6H_5.CH_2.C_6H_5$.

Cohen, Hirst (1895), *Chem. Soc. J.*, 67, 826.

60 grms. benzene.
30 ,, benzyl chloride.
1 ,, aluminium-mercury couple.

The benzene is placed in a flask attached to an upright condenser.* The couple (see p. 124) is then added, and the benzyl chloride dropped in slowly from a tap-funnel inserted through the top of the condenser. A brisk effervescence occurs, accompanied by a considerable rise of temperature, and fumes of hydrochloric acid are evolved. When, in the course of an hour, the benzyl chloride has been added, the flask is heated on the

water-bath for ten to fifteen minutes. The contents of the flask are now shaken up with water containing a little caustic soda, and the benzene solution separated in a tap-funnel. The aqueous portion is again extracted with benzene, and the whole of the benzene solution is dehydrated over calcium chloride. The benzene is then distilled off, and when the thermometer reaches 100° the distillation is continued *in vacuo*. At 80 mm. diphenyl-methane boils at 174—176°. This fraction solidifies completely on cooling, and is pure diphenylmethane; m. p. 25—26°. Yield, 14 grams.

$$C_6H_5CH_2Cl + C_6H_6 = C_6H_5CH_2C_6H_5 + HCl.$$
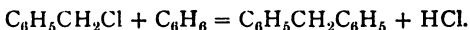
Properties.—Colourless needles; m. p. 26—27°; b. p. 263°. On boiling with potassium bichromate and sulphuric acid it is oxidised to benzophenone, $C_6H_5CH_2C_6H_5 + O_2 = C_6H_5.CO.C_6H_5 + H_2O.$

PREPARATION 89.

Triphenylmethane. $CH(C_6H_5)_3$.

Friedel, Crafts (1877), *Compt. rend.*, 1450; E. and O. Fischer (1878), *Ann.*, 197, 252; Biltz (1893), *Ber.*, 26, 1961.

> 200 grms. benzene.
> 40 ,, chloroform.
> 30 ,, aluminium chloride.

The benzene and chloroform are mixed together and dehydrated over calcium chloride overnight before use. The liquid is then decanted into a retort connected with an upright condenser,* and the powdered aluminium chloride added in portions of about 5 grams at a time at intervals of five minutes, and well shaken. On the addition of the chloride the reaction sets in spontaneously, and the liquid begins to boil with evolution of hydrochloric acid. The aluminium chloride gradually dissolves, forming a dark-brown liquid. The reaction is completed by boiling for half an hour on the sand-bath. When cold, the contents of the retort are poured into an equal volume of cold water, which decomposes the aluminium compound with evolution of heat, and the free hydrocarbon dissolves in the excess of benzene with a reddish-brown colour. The upper layer of benzene is separated from the aqueous portion, and the former

dehydrated over calcium chloride. The excess of benzene is distilled off on the water-bath, and the dark-coloured residue fractionated up to 200°. It is then distilled *in vacuo* from a retort without condenser.   At first an oil distils, which consists of impure diphenylmethane.   When most of the diphenyl compound has passed over, the distillation suddenly slackens. The receiver is now changed, and the retort more strongly heated.   An orange-coloured oil passes over, which crystallises in the receiver.   The distillation is continued until the distillate no longer solidifies on cooling.   A black resinous mass remains in the retort.   The crude triphenylmethane in the receiver is recrystallised from hot benzene, with which it forms a crystalline compound of the formula $C_{19}H_{16}.C_6H_6$.   This is again crystallised.   By heating the substance on the water-bath it loses benzene, and the hydrocarbon is finally crystallised from hot alcohol.   Yield, 25—30 grams.

$$CHCl_3 + 3C_6H_6 = CH(C_6H_5)_3 + 3HCl.$$
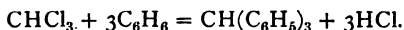
Properties.—Colourless plates ; m. p. 92° ; b. p. 360°.

Reactions.—Synthesis of Pararosaniline. Dissolve a gram of the hydrocarbon in about 5 c.c. cold fuming nitric acid, pour into water, filter, wash, dry on porous plate, and dissolve in 5 c.c. glacial acetic acid.   Add a gram of zinc dust on the point of a knife gradually, and shake up.   The colour changes to brown, and the leuco-base of pararosaniline is formed.   It is diluted with water and precipitated by ammonia.   It is then filtered and dried.   On gently warming the dry precipitate with a few drops of concentrated hydrochloric acid in a porcelain basin, a magenta colouration is produced from the formation of pararosaniline hydrochloride (E. and O. Fischer).

PREPARATION 90.

β-Naphthalenesulphonate of Sodium. $C_{10}H_7SO_3Na$.

Merz, Weith (1870), *Ber.*, 3, 196.

50 grms. naphthalene.
60   „   conc. sulphuric acid.

The mixture is heated in a round flask 250 c.c.) in the metal-bath to 170°—180° for four to five hours.   The liquid is then poured into a basin of water (1 litre), which is heated up and

neutralised with chalk or slaked lime in the form of a thick cream. The hot liquid is filtered through cloth, squeezed out, and washed with hot water. The filtrate is evaporated on a ring-burner until a sample crystallises on cooling. The crystalline mass of the calcium salt of naphthalene sulphonic acid is filtered and well pressed. It is redissolved in hot water, and a solution of sodium carbonate added, until the calcium is just precipitated. The liquid is again filtered through cloth, or at the pump, washed and well pressed. The filtrate is evaporated to crystallisation as before. The sodium naphthalene sulphonate is separated by filtration, and dried in a basin on the water-bath. The mother liquor, on evaporation, yields a further quantity of the salt. Yield, about 60 grams.

1. $C_{10}H_8 + H_2SO_4 = C_{10}H_7SO_3H + H_2O.$
2. $2C_{10}H_7SO_3H + CaO = (C_{10}H_7SO_3)_2Ca + H_2O.$
3. $(C_{10}H_7SO_3)_2Ca + Na_2CO_3 = 2C_{10}H_7SO_3Na + CaCO_3.$

Properties.—Foliated crystals ; soluble in water.


PREPARATION 91.

β-Naphthol. $C_{10}H_7.OH.$

Eller (1869), *Ann.*, 152, 275 ; E. Fischer, *Anleitung. z. d. org. Präparate.*

30 grms. β-naphthalene sulphonate of sodium.
90   „   caustic soda.
3 c.c. water.

The caustic soda and water are heated in a nickel or silver crucible, and stirred with a thermometer, protected as described under the preparation of phenol (p. 154). When the temperature reaches 280°, the powdered naphthalene sulphonate is added a little at a time. When all has been added, the temperature is raised. At about 300° the mass froths up and becomes light yellow in colour, which indicates the commencement of the reaction. The temperature is maintained at 310°—320° for a few minutes, and the end of the process is indicated by the yellow mass becoming thinner and also darker in colour, and

separating into two layers. The stirring is now stopped and the flame withdrawn. The product, when cold, is dissolved in a little water, and acidified with a mixture of equal volumes of concentrated hydrochloric acid and water.*

The naphthol is filtered off when cold, and is recrystallised from water. Yield, 15 grams.

$$C_{10}H_7SO_3Na + NaOH = C_{10}H_7ONa + NaHSO_3.$$
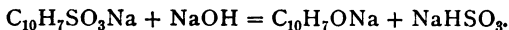
Properties.—Colourless leaflets, m. p. 123° ; b. p. 286°.

Reactions.—Add to a solution of the naphthol in water a few drops of ferric chloride. A green colouration is produced, and after a time a flocculent precipitate of dinaphthol, $C_{20}H_{14}O_2$.

See also Reaction 5, p. 141.

PREPARATION 92.

Anthraquinone. $C_6H_4\diagdown\diagup CO\diagup\diagdown C_6H_4.$
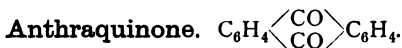
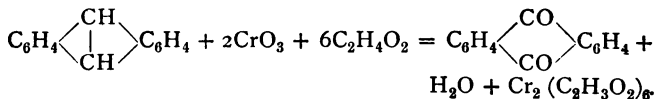Graebe, Liebermann (1869), *Ann. Spl.*, 7, 284.

  10 grms. anthracene (pure).
 120 c.c. glacial acetic acid.
  20 grms. chromium trioxide dissolved in 15 c.c. water, and then 75 c.c. glacial acetic acid added.

The anthracene is dissolved in the acetic acid by boiling them together in a round flask ($\frac{1}{2}$ litre) with upright condenser over wire-gauze. The solution of chromium trioxide is then dropped in from a tap-funnel pushed into the top end of the condenser whilst the liquid is kept boiling. The operation should last about an hour. The solution becomes a deep green. It is allowed to cool and poured into water (500 c.c.), which precipitates, the anthraquinone in the form of a brown powder. After standing an hour, it is filtered through a large fluted filter, washed with a little hot water, then with warm dilute caustic soda and water again. Yield 10—12 grams. A portion of the dry substance may be purified by sublimation. It is placed (2—3 grams) on a large watch-glass, which is heated on the sand-bath over a very small flame. The watch-glass is covered with a sheet of filter paper, which is kept flat by a funnel placed above. After five minutes

or so pale yellow, needle-shaped crystals of anthraquinone will have sublimed on to the filter paper.

$$C_6H_4 \underset{CH}{\overset{CH}{\diagdown}} C_6H_4 + 2CrO_3 + 6C_2H_4O_2 = C_6H_4 \underset{CO}{\overset{CO}{\diagup}} C_6H_4 +$$
$$H_2O + Cr_2(C_2H_3O_2)_6.$$

Properties.—Yellow needles; m. p. 277°; sublimes at 250°; b. p. 382°; insoluble in water, soluble in acetic acid, less soluble in benzene and other organic solvents.

Reaction.—Add a little dilute caustic soda to a small quantity of anthraquinone, and then a little zinc dust. On heating to boiling, an intense red colouration is produced, which disappears on shaking. Sodium oxanthranolate $C_6H_4 \underset{.CH(ONa)}{\overset{CO}{\diagdown}} C_6H_4$ is formed, which oxidises in the air to anthraquinone.

PREPARATION 93.

Anthraquinone β-monosulphonate of Sodium.

$$C_6H_4 \underset{CO}{\overset{CO}{\diagdown}} C_6H_3.SO_3Na + H_2O.$$
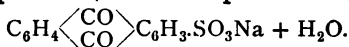
Graebe, Liebermann (1871), *Ann.*, 160, 131; A. G. Perkin. Private communication.

    30 grms. anthraquinone.
    30   „   fuming sulphuric acid (40 per cent. SO₃).[1]

The 40 per cent. fuming sulphuric acid is removed from the bottle by cautiously melting it in a sand-bath, and it is then weighed out in a flask (¼ litre). The anthraquinone is added, and the flask attached by a cork to an air-condenser. The mixture is heated in a paraffin or metal-bath to 150—160° for 8 hours. The dark coloured mass is poured *whilst hot* into a large basin containing about a litre of cold water, and boiled for an hour. The unattacked anthraquinone, which does not dissolve, is removed by filtration at the pump. The precipitate is then replaced in the basin and boiled up again with about

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[1] As fuming sulphuric acid is difficult to keep in an ordinary stoppered bottle without absorbing moisture, it is advisable to coat the stopper with a layer of paraffin wax, and a substantial covering of plaster of Paris above this.

½ litre of water, filtered and finally washed once or twice with boiling water. The combined filtrate and washings, which have a deep brown colour, are evaporated with the addition of ·2 gram of potassium chlorate until about ½ litre of liquid remains. It is now nearly neutralised with sodium carbonate solution (about 120 grams soda crystals) but not completely, as the sodium salt of the monosulphonic acid is less soluble in presence of acid. It is therefore convenient to pour out half a test-tube of the acid liquid, and proceed to neutralise the remainder. The small quantity of acid liquid is then replaced. The liquid is evaporated on the water-bath until a scum covers the surface, and it is then left to cool. The sodium salt of the sulphonic acid crystallises in pale yellow, silky crystals, and is separated at the pump. After being washed three or four times with a very little slightly acid water, it is dried on a porous plate. Yield, 20—25 grams. A further quantity of the salt may be obtained by evaporating the mother liquor, but it is liable to contain sodium sulphate.

$$C_{14}H_8O_2 + H_2SO_4 = C_{14}H_7O_2.SO_3H + H_2O.$$
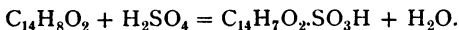
Properties.—The sodium salt of the sulphonic acid crystallises, when pure, in colourless leaflets, slightly soluble in cold water, insoluble in alcohol.

PREPARATION 94.

Alizarin. $C_6H_4 \diagup^{CO}_{CO} \diagdown C_6H_2 \diagup^{OH\ \ a}_{OH\ \ \beta}.$
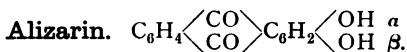
. Graebe, Liebermann (1869), *Ann. Spl.*, 300 ; Perkin (1869), *Engl. Patent*, No. 1948 ; A. G. Perkin. Private communication.

20 grms. anthraquinone monosulphonate of sodium.
       „   caustic soda.
  5 „   potassium chlorate.

The caustic soda is dissolved in about half its weight of water, and is added hot to the anthraquinone sulphonate of sodium, previously mixed into a paste with the potassium chlorate dissolved in about 50 c.c. of water. The mixture, which forms a stiff paste, is transferred at once to a small metal pressure tube of steel or phosphor-bronze of the shape and dimensions shown

in Fig 78.[1] The mixture fills it about two-thirds full. A sheet of asbestos cardboard is inserted between the body and the top of the vessel, and the metal top is then screwed firmly on. The pressure tube is heated for three hours in a paraffin or oil-bath, so that the thermometer inserted into the inner tube, which

9.5ᴄᴍ

12ᴄᴍ

5ᴄᴍ
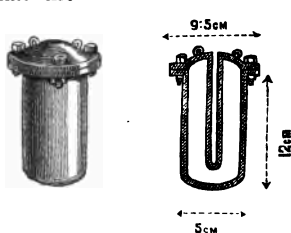
The thickness of the metal is 1 cm.

Fɪɢ. 78.

contains a little paraffin, registers 190—200°. The dark violet coloured mass, after cooling, is scraped out and digested with boiling water for an hour. Milk of lime is added until the violet calcium alizarate is all precipitated. This can be ascertained in a small filtered sample by adding a little milk of lime, when no violet pre-
cipitate should be formed. The precipitate is filtered at the pump and washed with boiling water until the filtrate is no longer red. The red filtrate contains a little monohydroxy-anthraquinone, which may be precipitated by hydrochloric acid. The calcium alizarate on the filter is suspended in a large quantity of hot water, and decomposed by adding hydro-chloric acid. The alizarin, which separates as an orange floc-culent precipitate, is filtered cold, washed about eight times with cold water, and finally dried and crystallised from alcohol or preferably cumene. Yield, 10—15 grams.

$$3C_{14}H_7O_2SO_3Na + 9NaOH + 2KClO_3 = 3C_{14}H_6O_2(ONa)_2 + 3Na_2SO_4 + 2KCl + 6H_2O.$$
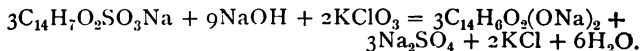
Properties. — Orange needles ; m. p. 289—290° ; sublimes completely at 140° without decomposition ; soluble in alkalis with a deep purple colour (sodium alizarate). It is reduced to anthracene on heating with dry zinc dust.

Reaction.—Make a small quantity of solution of alizarin in caustic soda, and pour into a beaker containing a strong solution of alum. The insoluble aluminium alizarate is precipitated as a red lake.

[1] The apparatus was made for us by West's Gas Improvement Co., Miles Platting, Manchester.

PREPARATION 95.

**Isatin from Indigo.** $C_6H_4\underset{N}{\overset{CO}{\diagdown}}C(OH)$.
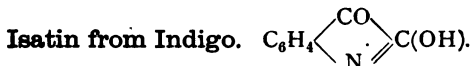
Erdmann (1841), *J. prakt. Ch.*, 24, 11 ; Knop (1865), *Jahresb.*, 580.

100 grms. indigo (in fine powder).
50 c.c. conc. nitric acid diluted with 10 c.c. water.

Mix up the indigo into a paste with 300 c.c. of boiling water in a large basin. Heat to boiling and remove the flame. Then add the nitric acid to the hot liquid from a tap-funnel at the rate of a drop or two a second, so that it is all added in the course of twenty minutes, and stir well all the time. The mass, which is at first pasty, froths up, and towards the end becomes thinner. Boil up for about two minutes, as soon as the acid has all been added, and then pour out about half the liquid into a second large basin and add a litre of boiling water to each. Boil up for five minutes, and decant from the floating lumps of tarry matter through a large fluted filter paper previously moistened with water. Add another litre of hot water to each basin, boil up, and filter. Evaporate the combined red coloured filtrates to about 1½ litre, and filter again, if necessary, from a further deposit of tar. On cooling, a quantity of red crystals discoloured with tar will separate. Filter and concentrate the filtrate. Redissolve the crystals in the smallest quantity of boiling water, and let the liquid cool somewhat, so that some of the tarry matter may separate ; filter and evaporate the filtrate, until crystals of isatin nearly cover the surface ; then cool and filter off the red crystalline deposit. A further quantity of crystals may be obtained by evaporating the mother-liquors, which must be frequently filtered from tarry deposit. The crystals obtained in this way may be purified by dissolving them in caustic potash solution, and adding concentrated hydrochloric acid to the clear liquid so long as a black precipitate is formed. The liquid is then filtered, and the purified isatin completely thrown down in the filtrate with more acid. The

substance is then filtered and recrystallised from water.   Yield, about 10 grams.

$$C_{16}H_{10}N_2O_2 + O_2 = 2C_8H_5NO_2.$$
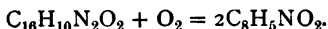
Properties.—Red monoclinic prisms ; m. p. 201° ; soluble in hot water and alcohol.

Reaction.—Dissolve a few crystals in concentrated sulphuric acid in the cold and shake up with a little coal-tar benzene.   A blue colour due to thiophene is produced.

PREPARATION 96.

Quinoline.
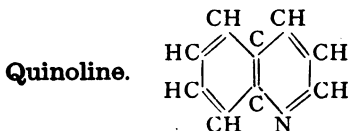
Skraup (1880), *Monatsh.*, 1, 316 (1881), 2, 141 ; König (1880), *Ber.*, 13, 911.

> 24 grms. nitrobenzene.
> 38   „   aniline.
> 120   „   glycerin.
> 100   „   conc. sulphuric acid.

A large round flask (1½—2 litres) is attached to an upright condenser.   The mixture of nitrobenzene, aniline, glycerin, and sulphuric acid, is poured in and heated on the sand-bath until the reaction sets in (ten to fifteen minutes) *i.e.* until white vapours rise from the liquid.   The flask is now raised from the sand-bath or the burner extinguished, and when the first reaction is over, the contents are gently boiled for two to three hours.   The dark coloured product is diluted with water, and unchanged nitrobenzene driven over with steam.   The residue is made strongly alkaline with caustic soda, and the oily layer (quinoline and aniline) distilled off with steam.   In order to remove the aniline present, the distillate is acidified with sulphuric acid, and sodium nitrite added, until a sample of the liquid ceases to give the aniline reaction with sodium hypochlorite.   It is then boiled, whereby the aniline is converted into phenol.   The

liquid is again made alkaline with caustic soda, and submitted to a third distillation with steam. The distillate is extracted with ether, dehydrated over solid caustic potash, and, after decanting and driving off the ether, the residue is distilled. Yield, 40 grams of a pale yellow oil.

$$C_6H_5NH_2 + C_3H_5(OH)_3 + O = C_9H_7N + 4H_2O.$$
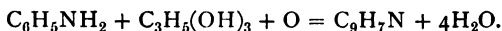
The sulphuric acid removes water, and the nitrobenzene acts as oxidising agent.

Properties.—Colourless liquid ; b. p. 237° ; sp. gr. 1·108 at 0° ; insoluble in water ; soluble in alcohol and ether,

Reactions.—1. Dissolve a few drops of quinoline in a little hydrochloric acid and add platinic chloride. Orange crystals of the chloroplatinate are deposited $(C_9H_7N)_2H_2PtCl_6 + H_2O.$

2. Add to a solution of quinoline in acid, potassium chromate solution ; the bichromate, $(C_9H_7N)_2H_2Cr_2O_7$, is precipitated.

3. Add to 1 c.c. of quinoline, 1 c.c. of methyl iodide, and warm. A reaction sets in, and, on cooling, the quaternary ammonium iodide, $C_9H_7N.CH_3I$, crystallises in yellow crystals.

4. To a few drops of quinoline add a solution of bromine in chloroform. A crystalline compound, $C_9H_7N.Br_2$, is formed.

PREPARATION 97.

Quinine Sulphate from Cinchona Bark.
$$C_{20}H_{21}N_2O_2.SO_4H_2 + 8H_2O.$$

Pelletier, Caventou (1820), *Ann. Ch. Phys.* (2), 15, 291.

100 grms. cinchona bark (ground in a coffee mill).
20   „   quicklime.

Slake the quicklime, and mix it into a thin cream with 200 c.c. water. Pour the liquid into a basin containing the powdered bark and stir up the mass well. Dry the mixture thoroughly on the water-bath, taking care to powder up the lumps that ball together. When cold, pour the powder into a flask and on to it 200 c.c. chloroform, and let the mixture stand over night. Filter through a porcelain funnel and wash with a further 200 c.c. chloroform. The chloroform solution, which

has now a faint yellow colour, is shaken up well with 50 c.c. and again with 25 c.c. dilute sulphuric acid, and then with water until the aqueous solution has no longer a blue fluorescence. The combined acid and aqueous extracts are carefully neutralised with ammonia, and the liquid concentrated on the water-bath until crystals of quinine sulphate begin to form on the surface. The liquid is allowed to cool and filtered. A further quantity of crystals may be obtained from the mother-liquor by evaporation, but the product is not so pure. The crystals are purified by recrystallisation from water. Yield, 1 to 2 grams, or more, according to the quality of the bark.

Properties.--The free base, which is precipitated with sodium carbonate from a solution of its salts, crystallises with $3H_2O$. The anhydrous base melts at 277°; soluble in alcohol and ether.

Reactions.—Use a solution of the hydrochloride prepared by adding a few drops of hydrochloric acid to the sulphate mixed with water.

1. Add to a little of the solution a few drops of iodine solution ; a brown amorphous precipitate is formed. This reaction is given by many of the alkaloids.

2. Add chlorine water and then ammonia in excess. An emerald green colouration is produced.

3. Add sodium carbonate solution and then shake with ether. The free base is precipitated and dissolves in the ether. Decant the ether on to a watch-glass and let it evaporate. Crystals of the base remain.
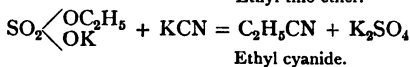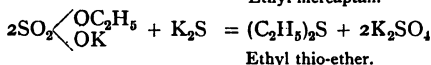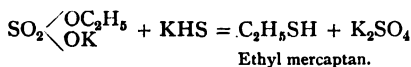
4. Dissolve in a few drops of acetic acid and add a large volume of water. A blue fluorescent liquid is obtained.

# APPENDIX

NOTES ON THE PREPARATIONS

PREPARATION 1.

Ethyl Potassium Sulphate.—The combination between alcohol and sulphuric acid is not complete, a condition of equilibrium being reached before either constituent is completely converted. The free alkyl acid sulphates are, as a rule, viscid liquids, which cannot be distilled without yielding the olefine. On boiling with water, the alcohol is regenerated. The salts are used for preparing various alkyl derivatives, such as mercaptans, thio-ethers and cyanides.

$$SO_2 {\diagup OC_2H_5 \atop \diagdown OK} + KHS = C_2H_5SH + K_2SO_4$$
$$\text{Ethyl mercaptan.}$$

$$2SO_2 {\diagup OC_2H_5 \atop \diagdown OK} + K_2S = (C_2H_5)_2S + 2K_2SO_4$$
$$\text{Ethyl thio-ether.}$$

$$SO_2 {\diagup OC_2H_5 \atop \diagdown OK} + KCN = C_2H_5CN + K_2SO_4$$
$$\text{Ethyl cyanide.}$$

Compare the action of sulphuric acid on phenol, (see Prep. 72, p. 157).

PREPARATION 2.

Ethyl Bromide.—The replacement of the hydrogen by halogen (Cl, Br) may be effected by the direct action of the halogen on the paraffin.

$$C_2H_6 + Cl_2 = C_2H_5Cl + HCl.$$
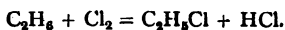
A simpler method is to replace the alcohol *hydroxyl* by halogen by the action of hydracid (HCl, HBr, HI),

$$C_2H_5OH + HCl = C_2H_5Cl + H_2O.$$
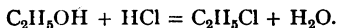
Or by that of the phosphorus compound (PCl$_3$, PBr$_3$, PI$_3$),

$$3C_2H_5OH + PCl_3 = 3C_2H_5Cl + P(OH)_3.$$
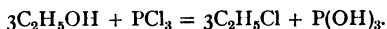
The preparation of ethyl bromide may be taken as an example of the first method, in which the hydracid is liberated by the reaction,

$$KBr + H_2SO_4 = HBr + KHSO_4.$$
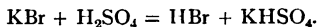
A further example is that of isopropyl iodide, see Prep. 28, p. 97, in which the hydriodic acid is obtained by the action of water on phosphorus iodide,

$$PI_3 + 3H_2O = 3HI + P(OH)_3.$$
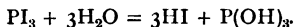
The action of HCl is much more sluggish than that of HBr or HI, and in the preparation of ethyl chloride a dehydrating agent (ZnCl$_2$) is usually added to the alcohol, which is kept boiling whilst the HCl gas is passed in. In the case of polyhydric alcohols, all the hydroxyl groups cannot be replaced by Cl by the action of HCl. Glycol gives ethylene chlorhydrin and glycerin yields the dichlorhydrin, (see Prep. 29, p. 98). The use of PBr$_3$, PI$_3$ does not necessitate the previous preparation of these substances. Amorphous phosphorus is mixed with the alcohol, and bromine or iodine added as in the preparation of methyl iodide, (see Prep. 6, p. 61). PCl$_5$, or PCl$_3$ will always replace OH by chlorine in all hydroxy-compounds, including phenols, on which HCl does not act.

The alkyl halides are utilised in a variety of reactions, examples of which are given, ethyl iodide being taken as the type.
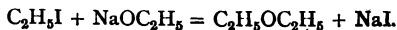
1. *Aqueous* potash or water with metallic oxide (Ag$_2$O, PbO) yields the alcohol (see Prep. 78, p. 166),
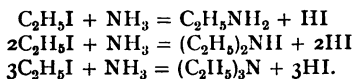
$$C_2H_5I + KOH = C_2H_5OH + KI.$$
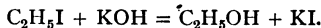
2. *Alcoholic* potash gives an olefine,

$$C_2H_5I + KOH = C_2H_4 + KI + H_2O.$$
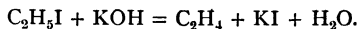
3. Sodium alcoholate gives an ether,

$$C_2H_5I + NaOC_2H_5 = C_2H_5OC_2H_5 + NaI.$$

4. Alcoholic ammonia forms a mixture of primary, secondary and tertiary amines,

$$C_2H_5I + NH_3 = C_2H_5NH_2 + HI$$
$$2C_2H_5I + NH_3 = (C_2H_5)_2NH + 2HI$$
$$3C_2H_5I + NH_3 = (C_2H_5)_3N + 3HI.$$

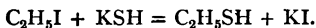The tertiary amines unite with the alkyl iodide to form the quaternary ammonium iodide, which is produced at the same time as the other products.

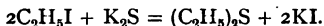$$(C_2H_5)_3N + C_2H_5I = (C_2H_5)_4NI.$$
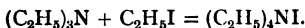
5. Potassium cyanide forms alkyl cyanide,

$$C_2H_5I + KCN = C_2H_5CN + KI.$$
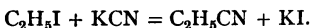
6. Potassium sulph-hydrate gives the mercaptan,

$$C_2H_5I + KSH = C_2H_5SH + KI.$$

7. Potassium sulphide forms the thio-ether,

$$2C_2H_5I + K_2S = (C_2H_5)_2S + 2KI.$$

8. Silver nitrite gives the nitro-paraffin,

$$C_2H_5I + AgNO_2 = C_2H_5NO_2 + AgI.$$
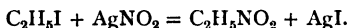
9. Silver salts of organic or inorganic acids yield the alkyl esters,

$$2C_2H_5I + Ag_2SO_4 = (C_2H_5)_2SO_4 + 2AgI.$$
$$C_2H_5I + CH_3.COOAg = CH_3.COOC_2H_5. + AgI.$$
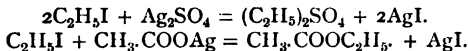
PREPARATION 3.

Ethyl Ether.—This reaction is of a general character. By using a different alcohol in the reservoir from that in the flask, a *mixed* ether may be obtained. Thus, ethyl alcohol and amyl alcohol may be combined to form ethyl amyl ether,

$$C_2H_5OH + H_2SO_4 = C_2H_5SO_4H + H_2O.$$
$$C_2H_5HSO_4 + C_5H_{11}OH = C_2H_5OC_5H_{11} + H_2SO_4.$$
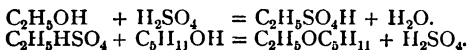
The ethers are also formed by the action of sodium alcoholate on the alkyl iodide (Williamson),

$$C_2H_5ONa + C_2H_5I = C_2H_5.O.C_2H_5 + NaI,$$
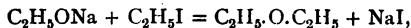
and by this method mixed ethers may also be prepared.

That the ethers are inert bodies arises probably from the

fact that the whole of the hydrogen present is united to carbon. Note the action of sodium and PCl_5 on alcohol and on ether. The ethers are not decomposed with PCl_5 except on heating, when they give the alkyl chlorides,
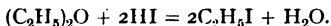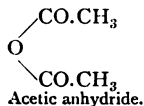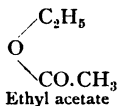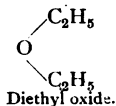
$$(C_2H_5)_2O + PCl_5 = 2C_2H_5Cl + POCl_3.$$
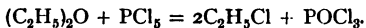
Hydracids, especially H I, have a similar action—

$$(C_2H_5)_2O + 2HI = 2C_2H_5I + H_2O.$$

Compare the action of caustic alkalis on ethers, esters and anhydrides.

∕C₂H₅ O ∖C₂H₅ Diethyl oxide.	∕C₂H₅ O ∖CO.CH₃ Ethyl acetate	∕CO.CH₃ O ∖CO.CH₃ Acetic anhydride.

PREPARATION 4.

Ethylene Bromide.— The formation of olefines by the action of conc. H_2SO_4 and other dehydrating agents on the alcohols is a very general reaction. Among the higher alcohols the action of heat alone suffices ; cetyl alcohol, $C_{16}H_{34}O$, gives cetylene $C_{16}H_{32}$ on heating. The olefines are also obtained by the action of alcoholic potash on the alkyl bromides and iodides,

$$C_2H_5Br + KOH = C_2H_4 + KBr + H_2O,$$

and by the electrolysis of the dibasic salts ; potassium succinate gives ethylene,

$$C_2H_4(COOK)_2 = C_2H_4 + 2CO_2 + K_2(H_2).$$
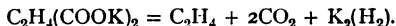
The olefines combine with :

(1) Hydrogen in presence of platinum black,

$$CH_2 : CH_2 + H_2 = CH_3.CH_3.$$
$$\text{Ethylene.} \qquad\qquad \text{Ethane.}$$
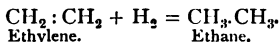
(2) The hydracids (HCl, HBr, HI), in which case the halogen attaches itself to the carbon with the least number of hydrogen atoms,

$$CH_3.CH : CH_2 + HI = CH_3.CHI.CH_3.$$
$$\text{Propylene.} \qquad\qquad \text{Isopropyl iodide.}$$

(3) The halogens (Cl,Br,I),

$$CH_2 : CH_2 + Cl_2 = CH_2Cl.CH_2Cl.$$
$$\text{Ethylene.} \qquad\qquad \text{Ethylene chloride.}$$

(4) Conc. sulphuric acid,

$$CH_2 : CH_2 + O_2S\begin{matrix}OH\\OH\end{matrix} = O_2S\begin{matrix}OCH_2.CH_3\\OH\end{matrix}$$
$$\text{Ethyl hydrogen sulphate.}$$

(5) Hypochlorous acid,

$$CH_2 : CH_2 + HOCl = CH_2OH.CH_2Cl.$$
$$\text{Ethylene chlorhydrin.}$$
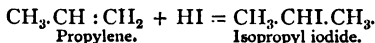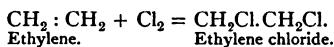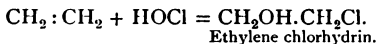
Potassium permanganate oxidises the olefine, forming in the first stage the corresponding glycol. By further oxidation the molecule is decomposed by the parting of the carbon atoms at the original double link,

$$CH_3.CH : CH_2 + H_2O + O = CH_3.CHOH.CH_2OH.$$
$$\text{Propylene.} \qquad\qquad \text{Propylene glycol.}$$
$$CH_3.CHOH.CH_2OH + 2O_2 = CH_3.COOH + CO_2 + 2H_2O.$$
$$\text{Acetic acid.}$$
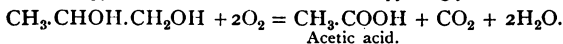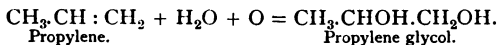
Alkylene chlorides and bromides with both halogen atoms attached to the same carbon are obtained by the action of PCl_5, and PBr_5 on aldehydes and ketones.

$$CH_3.CO.CH_3 + PCl_5 = CH_3.CCl_2.CH_3 + POCl_3.$$
$$\beta\beta\text{-dichloropropane.}$$
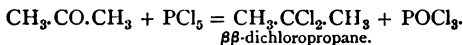
PREPARATION 5.

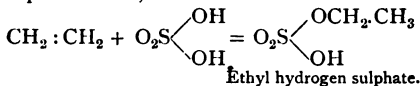**Acetaldehyde.**--The formation of aldehyde from alcohol probably occurs by the addition of oxygen and subsequent elimination of water,

$$CH_3CH_2OH + O = CH_3.CH(OH)_2 = CH_3.CO.H + H_2O.$$
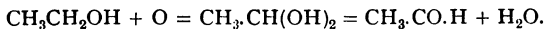
The aldehydes may also be obtained by the reduction of acid chlorides and of anhydrides in some cases, but the method is rarely adopted. Aldehydes can only be obtained directly from the fatty acids by distilling the calcium salt with calcium form-ate ; but in no case by direct reduction, unless in the form of lactones,

$$(CH_3.COO)_2Ca + (HCOO)_2Ca = 2CH_3.CO.H + 2CaCO_3.$$

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The aldehydes are readily reduced to the alcohols. Characteristic properties of the aldehydes are the formation of aldehyde ammonias, Schiff's reaction, the reduction of metallic salts and the production of *acetals* by the action of alcohol in presence of hydrochloric acid gas (E. Fischer).

$$CH_3.CO.H + 2C_2H_5OH = CH_3.CH(OC_2H_5)_2 + H_2O.$$
$$\text{Acetal.}$$
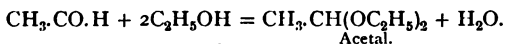
They also polymerise readily. These reactions should be compared with those of benzaldehyde (Prep. 79, p. 167). There are many reactions which are common to both aldehydes and ketones, *i.e.*, to all substances which contain a ketone $>$CO group. Such, for example, are : (1) The formation of an additive compound with sodium bisulphite.

$$>CO + NaHSO_3 = >C<^{OH}_{SO_3Na}$$
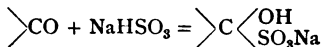
(2) The action of PCl_5 which replaces oxygen by chlorine,

$$>CO + PCl_5 = >CCl_2 + POCl_3.$$
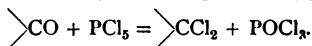
(3) The formation of a cyanhydrin with hydrocyanic acid,

$$>CO + HCN = >C<^{OH}_{CN},$$
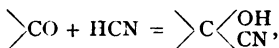
which on hydrolysis yields an oxy-acid.

(4) The formation of an oxime with hydroxylamine (see Preps. 9, p. 64, and 87, p. 176).

$$>CO + H_2NOH = >C:NOH + H_2O.$$
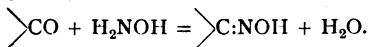
(5) The formation of a phenylhydrazone with phenylhydrazine (see Preps. 41, p. 120, and 64, p. 150).

$$>CO + H_2N.NH.C_6H_5 = >C:N.NHC_6H_5 + H_2O.$$
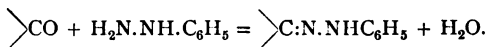
(6) The formation of a semicarbazone with semicarbazide (see Prep. 87, p. 176).

$$>CO + H_2N.NH.CO.NH_2 = >C:N.NH.CONH_2 + H_2O.$$
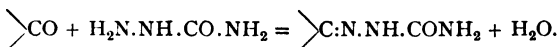
Both aldehydes and ketones readily undergo *condensation,* and a great variety of syntheses have been effected in this way (see Preps. 81, p. 169, and 82, p. 171).

The aldehydes unite with zinc methyl to form additive compounds, which decompose with water, yielding secondary alcohols (Butlerow).

$$CH_3.CO.H + Zn(CH_3)_2 = CH_3.C\!\!<\!\!\begin{array}{l}OZnCH_3\\H\\CH_3\end{array}$$

$$CH_3.C\!\!<\!\!\begin{array}{l}OZnCH_3\\H\\CH_3\end{array} + H_2O = CH_3.CHOH.CH_3 + ZnO + CH_4.$$
$$\text{Isopropyl alcohol.}$$
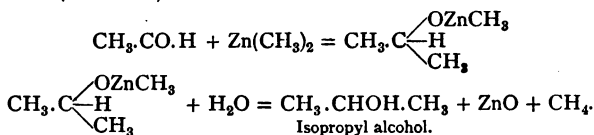
Acetaldehyde, in presence of HCl, polymerises, forming aldol. With zinc chloride the reaction goes a step further and crotonaldehyde is formed,

$$CH_3.COH + CH_3.COH = CH_2.CH(OH).CH_2.COH.$$
$$\text{Aldol.}$$

$$CH_3.CHOH.CH_2.COH = CH_3.CH\!:\!CH.COH + H_2O.$$
$$\text{Crotonaldehyde.}$$
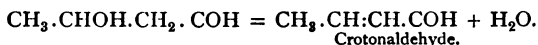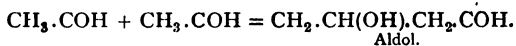
PREPARATION 6.

Methyl Iodide.—Read notes on Prep. 2, p. 189.

PREPARATION 7.

Amyl Nitrite.—The nitrites of the general formula R'.O.NO are isomeric with the nitro-paraffins R'NO$_2$. Whereas the nitrites are hydrolysed with KOH like other esters into the alcohol and the acid,

$$C_2H_5ONO + KOH = C_2H_5OH + KNO_2,$$
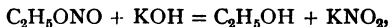
and are decomposed by reducing agents into the alcohol and ammonia (and in some cases hydroxylamine), the nitro-paraffins are not hydrolysed by potash, but dissolve, forming the soluble potassium salt, and on reduction give the primary amine,

$$C_2H_5NO_2 + 3H_2 = C_2H_5NH_2 + 2H_2O.$$
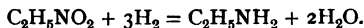
Amyl nitrite is used in the preparation of diazo salts (see Prep. 57, p. 140).

PREPARATION 10.

Acetyl Chloride.—Either PCl$_3$ or PCl$_5$ are almost invariably used in the preparation of acid chlorides. In the case of PCl$_5$ only a portion of the chlorine of the reagent is utilised

(see Prep. 85, p. 173), $POCl_3$ being produced in the reaction. The use of one or other reagent is determined by the nature of the product. If the latter has a low boiling-point the trichloride is preferred, if a high boiling-point, the pentachloride may be used and the oxychloride expelled by distilling *in vacuo* from a water-bath (see Prep. 85, p. 173). The pentachloride is more frequently used in the preparation of aromatic acid chlorides, but there are occasions, which experience can only determine, when the trichloride is preferable. Acid chlorides react with alcohols and phenols, and in general with substances containing a "hydroxyl" (OH) group. Acetic anhydride has a similar behaviour, and both substances may be used in determining the number of such groups in a compound. Thus glycerin forms a triacetyl derivative, whilst glucose yields a pentacetyl compound. By hydrolysing the acetyl derivative with alkali, and then estimating the amount of alkali neutralised by titration, the number of acetyl groups can be estimated.

The presence of the "amido" (NH_2) group is determined by a similar reaction.

The synthesis of aromatic ketones may be effected with the acid chlorides, using Friedel and Crafts' reaction (see Prep. 87, p. 175), also of aliphatic ketones and tertiary alcohols with zinc methyl and ethyl, &c. (Butlerow).

$$(1)\quad CH_3.COCl + Zn(CH_3)_2 = CH_3.C{\overset{\displaystyle OZnCH_3}{\underset{\displaystyle CH_3}{\big\langle}}}Cl$$

$$CH_3.C{\overset{\displaystyle OZnCH_3}{\underset{\displaystyle CH_3}{\big\langle}}}Cl + H_2O = \underset{\text{Acetone.}}{CH_3.CO.CH_3} + Zn{\big\langle}{\overset{\displaystyle Cl}{\underset{\displaystyle OH}{}}} + CH_4.$$

$$(2)\quad CH_3.COCl + 2Zn(CH_3)_2 = CH_3.C{\overset{\displaystyle OZnCH_3}{\underset{\displaystyle CH_3}{\big\langle}}}CH_3 + Zn{\big\langle}{\overset{\displaystyle CH_3}{\underset{\displaystyle Cl}{}}}$$

$$CH_3.C{\overset{\displaystyle OZnCH_3}{\underset{\displaystyle CH_3}{\big\langle}}}CH_3 + H_2O = \underset{\text{Tertiary butyl alcohol.}}{CH_3.C(OH)(CH_3)_2} + ZnO + CH_4$$
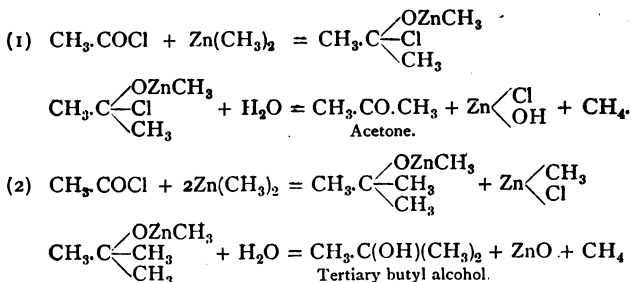
An additive compound with zinc methyl is formed, in the first reaction with one molecule, in the second with two molecules, and the product in each case is then decomposed with water.

PREPARATION 11.

Acetic Anhydride.—The anhydrides may be regarded as oxides of the acid radicals, just as ethers are the oxides of the alcohol radicals, and, like the ethers, both simple and mixed anhydrides may be prepared. The latter, however, on distillation decompose, giving a mixture of the simple anhydrides.

$$2{C_2H_3O \atop C_5H_9O}\!\!\Big\rangle O = {C_2H_3O \atop C_2H_3O}\!\!\Big\rangle O + {C_5H_9O \atop C_5H_9O}\!\!\Big\rangle O.$$
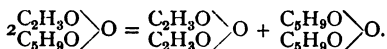
Anhydrides may also be prepared by the action of $POCl_3$ on the potassium salt of the acid in presence of excess of the latter, the reaction occurring in two phases :

$$2CH_3.COOK + POCl_3 \;\; = 2CH_3.COCl + KPO_3 + KCl.$$
$$CH_3.COOK + C_2H_3OCl = (C_2H_3O)_2O + KCl.$$
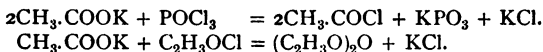
In addition to the reactions described under the Preparation, the anhydrides undergo the following changes :

1. With HCl, HBr, and HI they give, on heating, the acid chloride and free acid,

$$(CH_3CO)_2O + HCl = CH_3COCl + CH_3.COOH.$$

2. With Cl they form acid chloride and chlorinated acid,

$$(CH_3CO)_2O + Cl_2 = CH_3COCl + CH_2.Cl.COOH.$$

3. With Na amalgam they are reduced to aldehydes.

PREPARATION 12.

Acetamide.—The acid amides, or simply amides, correspond to the amines, being ammonia in which hydrogen is replaced by acid radicals, and, like the amines, exist in the form of primary secondary and tertiary amides. The following methods are used for obtaining the amides, in addition to that described under the preparation :

1. The action of ammonia on the acid chlorides or anhydrides. (See Prep. 85, p. 174.)

$$CH_3.CO.Cl + 2NH_3 = CH_3.CO.NH_2 + NH_4Cl.$$

$${CH_3.CO \atop CH_3.CO}\!\!\Big\rangle O + 2NH_3 = CH_3.CO.NH_2 + CH_3.COONH_4.$$
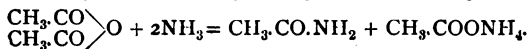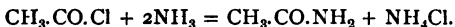
2. The action of ammonia on the esters. (See Prep. 24, p. 91)

$$CH_3.COOC_2H_5 + NH_3 . = CH_3.CONH_2 + C_2H_5OH.$$
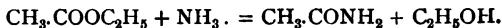
3. Partial hydrolysis of the cyanides by conc. hydrochloric or sulphuric acid,

$$CH_3.CN + H_2O = CH_3.CONH_2.$$
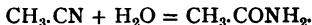
The alkyl amides or substituted ammonias, with both acid and alkyl radicals, also exist, and are formed by the first two of the above reactions and by heating the salt of the amine. (See Prep. 49, p. 131.)

$$CH_3.CO.Cl + NH_2C_2H_5 = CH_3.CO.NHC_2H_5 + HCl.$$
<div align="center">Acetethylamide.</div>

$$CH_3.COOH.NH_2C_6H_5 = CH_3.CONH.C_6H_5 + H_2O$$
<div align="center">Aniline acetate.   Acetanilide.</div>
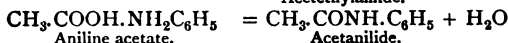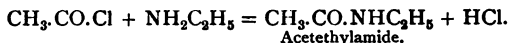
With the exception of formamide, which is a viscid liquid, the majority of these compounds are crystalline solids. The lower members are soluble in water, and they all dissolve in alcohol or ether. Many of them distil without decomposition. They are neutral substances uniting with both mineral acids and a few of them with caustic alkalis and alkaline alcoholates to form compounds, which are rapidly decomposed by water.

The hydrogen of the amido-group is also replaceable by metals, and derivatives of acetamide of the following formulæ are known :

$$CH_3.CONHNa, \quad CH_3.CONHAg, \quad (CH_3.CO.NH)_2Hg.$$

They are converted by nitrous acid into the organic acid, and in the case of substituted amides into nitrosamides,

$$CH_3CONH_2 + HNO_2 \quad = CH_3.CO.OH + N_2 + H_2O.$$
$$CH_3.CO.NHC_6H_5 + HNO_2 = CH_3.CO.N(NO).C_6H_5 + H_2O.$$
<div align="center">Acetanilide.   Nitrosoacetanilide.</div>
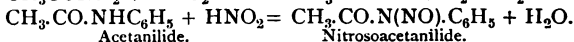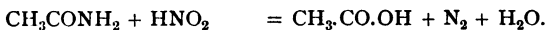
With the latter class of substituted amides PCl$_5$ forms the imidochlorides, a reaction, which is usually formulated in two steps,

$$CH_3.CO.NHC_6H_5 + PCl_5 = CH_3.CCl_2.NHC_6H_5 + POCl_3.$$
$$CH_3.CCl_2.NHC_6H_5 = CH_3CCl:NC_6H_5 + HCl.$$
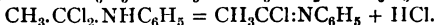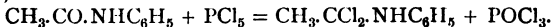
The unsubstituted amides give both imidochloride and the cyanide with PCl$_5$,

$$CH_3.CONH_2 + PCl_5 = CH_3.C\!\!\diagup^{NH}_{Cl} + POCl_3 + HCl.$$

$$CH_3.C\!\!\diagup^{NH}_{Cl} = CH_3.CN + HCl.$$
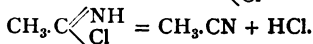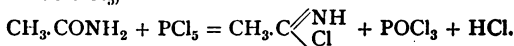
PREPARATION 13.

Acetonitrile.—The various reactions by which the nitriles or alkyl cyanides are obtained have already been mentioned in one or other of the previous notes, but they may be recapitulated.

1. By the action of KCN on the alkyl iodide or alkyl potassium sulphate.

$$C_2H_5I + KCN = C_2H_5CN + KI.$$
$$SO_2\hspace{-2pt}\big\langle {}^{OC_2H_5}_{OK} + KCN = C_2H_5CN + K_2SO_4.$$
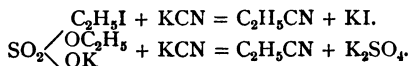
2. By the action of PCl_5 (as well as P_2O_5) on the amide,

$$CH_3 . CONH_2 + PCl_5 = CH_3CN + POCl_3 + 2HCl.$$
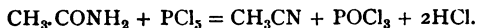
3. By heating the aldoxime with acetic anhydride,

$$CH_3 . CH : NOH + (CH_3CO)_2O = CH_3CN + 2CH_3 . COOH.$$
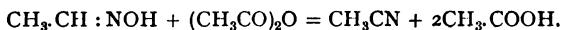
They are compounds which are, for the most part, insoluble in water, possess an ethereal smell, have a neutral reaction, and may be distilled.

The fact that they are eminently unsaturated compounds is evidenced by their general behaviour towards a great variety of reagents.

1. On reduction they give the primary amine (Mendius).

$$CH_3CN + 2H_2 = CH_3CH_2NH_2.$$
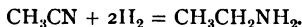
2. With HCl, HBr, and HI they form imidohalides (Wallach),

$$CH_3CN + HCl = CH_3 . C\hspace{-2pt}\big\langle {}^{NH}_{Cl}.$$
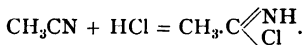
3. With alcohol and HCl they form the hydrochloride of the imidoethers, from which caustic alkali liberates the base (Pinner),

$$CH_3CN + C_2H_5OH + HCl = CH_3 . C\hspace{-2pt}\big\langle {}^{NH.HCl}_{OC_2H_5}.$$

$$CH_3 . C\hspace{-2pt}\big\langle {}^{NH.HCl}_{OC_2H_5} + NaOH = CH_3 . C\hspace{-2pt}\big\langle {}^{NH}_{OC_2H_5} + NaCl + H_2O.$$
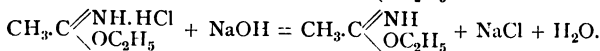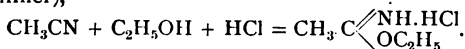
These imidoethers unite with ammonia and amines and form the amidines,

$$CH_3 . C\hspace{-2pt}\big\langle {}^{NH}_{OC_2H_5} + NH_3 = CH_3 . C\hspace{-2pt}\big\langle {}^{NH}_{NH_2} + C_2H_5OH.$$

Acetamidine.
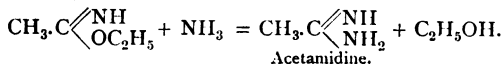
4. The latter are also formed by the direct action of ammonia on the cyanide,

$$CH_3.CN + NH_3 = CH_3.C{\diagup}^{NH}_{\diagdown NH_2}.$$
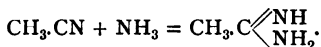
5. Hydroxylamine unites with the cyanides forming amid-oximes,

$$CH_3.CN + NH_2OH = CH_3.C{\diagup}^{NOH}_{\diagdown NH_2}.$$
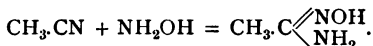
6. With H_2S the thiamides are formed,

$$CH_3.CN + H_2S = CH_3.CS.NH_2.$$
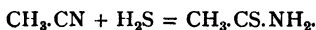
PREPARATION 14.

Methylamine hydrochloride.—This reaction, which yields the primary amine, is applicable not only to the aliphatic but also to the aromatic amides. The formation of anthranilic acid from phthalimide is a process of technical importance. By the action of bromine and caustic potash, phthalaminic acid is first formed, which then yields the amido acid,

$$C_6H_4{\diagup}^{CO}_{\diagdown CO}{\diagdown}NH + H_2O = C_6H_4{\diagup}^{CONH_2}_{\diagdown COOH}$$

$$C_6H_4{\diagup}^{CONH_2}_{\diagdown COOH} + Br = C_6H_4{\diagup}^{CONHBr}_{\diagdown COOH} + HBr.$$

$$C_6H_4{\diagup}^{CONHBr}_{\diagdown COOH} = C_6H_4{\diagup}^{NCO}_{\diagdown COOH} + HBr.$$

$$C_6H_4{\diagup}^{NCO}_{\diagdown COOH} + H_2O = C_6H_4{\diagup}^{NH_2}_{\diagdown COOH} + CO_2.$$
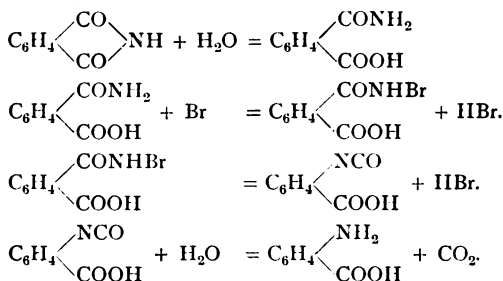
The primary amines may also be obtained by the following reactions :

1. Action of alcoholic ammonia on the alkyl iodides and nitrates,

$$C_2H_5I + NH_3 = C_2H_5NH_2 + HI. \quad \text{(Hofmann.)}$$

Secondary and tertiary amines are also formed (see p. 191),

$$C_2H_5ONO_2 + NH_3 = C_2H_5NH_2 + HNO_3. \quad \text{(Wallach.)}$$
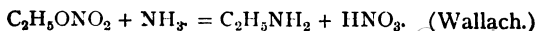
2. Reduction of the following classes of compounds :

> nitro-compounds
> cyanides
> oximes
> phenylhydrazones

$$C_2H_5NO_2 + 3H_2 = C_2H_5NH_2 + 2H_2O. \quad \text{(V. Meyer.)}$$
$$C_2H_5CN + 2H_2 = C_2H_5CH_2NH_2. \quad \text{(Mendius.)}$$
$$CH_3.CH:NOH + 2H_2 = CH_3.CH_2.NH_2 + H_2O. \quad \text{(Goldschmidt.)}$$
$$CH_3.CH:N.NHC_6H_5 + 2H_2 = CH_3.CH_2.NH_2 + C_6H_5.NH_2. \quad \text{(Tafel.)}$$
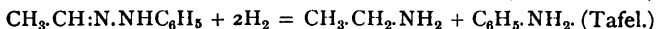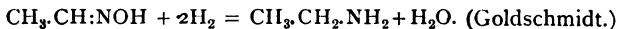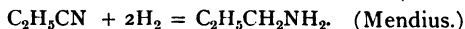
3. Hydrolysis of the isocyanides with conc. HCl,

$$C_2H_5NC + 2H_2O = C_2H_5NH_2 + HCO.OH.$$
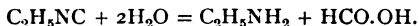
The three classes of aliphatic amines (primary, secondary, and tertiary) may be distinguished by their behaviour with nitrous acid and alkyl iodide. The primary amine is decomposed with HNO_2 forming the alcohol, and nitrogen is evolved,

$$C_2H_5NH_2 + HNO_2 = C_2H_5OH + N_2 + H_2O.$$
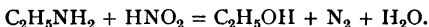
The secondary amine forms the nitrosamine, insoluble in water,

$$(C_2H_5)_2NH + HNO_2 = (C_2H_5)_2N.NO + H_2O.$$
<div align="center">Diethylnitrosamine.</div>
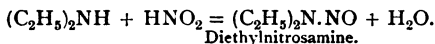
The tertiary amine is unacted on by nitrous acid, but, unlike the other two, unites with an alkyl iodide and forms the quaternary ammonium iodide (Hofmann),

$$(C_2H_5)_3N + CH_3I = (C_2H_5)_3NCH_3I.$$
<div align="center">Triethylmethylammonium iodide.</div>
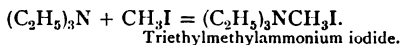
The behaviour of nitrous acid with the aromatic amines is somewhat different (See Preps. 53, p. 134, and 57, p. 140).

PREPARATION 15.

Ethyl acetate.—Esters may be obtained by the direct action of the alcohol on the acid as in the case of methyl oxalate. (Prep. 24, p. 90). A certain quantity of ethyl acetate is also obtained from ethyl alcohol and acetic acid, but the action, which is known as a *reversible* one, stops when a certain proportion of the constituents have combined. It is represented thus :

$$C_2H_5OH + CH_3.COOH \rightleftarrows CH_3.COOC_2H_5 + H_2O,$$
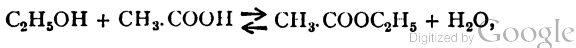
which signifies that the ester and water react and regenerate
alcohol and acid, whilst the reverse process is in operation.   By
removing the water as it is formed by means of sulphuric acid
or by distillation, this condition of equilibrium is disturbed and
the reaction is completed.   This does not however explain the
fact, first discovered by Scheele and afterwards investigated by
Fischer and Speier (see Prep. 86, p. 174), that a very limited
quantity of conc. sulphuric or hydrochloric acid will produce
the same result.   According to Henry the reaction with HCl
takes place in several steps,

$$CH_3.COOH + C_2H_5OH = CH_3C(OH)_2OC_2H_5.$$
$$CH_3.C(OH)_2OC_2H_5 + HCl = CH_3C(OH)ClOC_2H_5 + H_2O.$$
$$CH_3.C(OH)ClOC_2H_5 = CH_3.COOC_2H_5 + HCl.$$
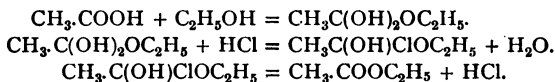
Other methods for the preparation of esters are by the action of
alcohol on the acid chloride or anhydride (see Reactions, p. 68),
or by boiling up the dry powdered silver salt of the acid with the
alkyl iodide,

$$CH_3.COOAg + C_2H_5I = CH_3.COOC_2H_5 + AgI.$$
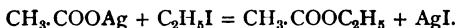
The esters are, for the most part, colourless liquids or solids of
low m. p., with a fruity smell and insoluble in water.   They are
hydrolysed by potash (most readily with alcoholic potash) and
give amides with ammonia,

$$CH_3.COOC_2H_5 + NH_3 = CH_3.CONH_2 + C_2H_5OH.$$
$$\text{Acetamide.}$$
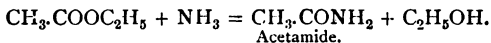
PREPARATION 16.

Ethyl acetoacetate.—The explanation of the manner in
which this substance is produced has been given in the account
of the preparation.   The result was arrived at not by the isola-
tion of the intermediate compound formed by the union of
ethyl acetate with sodium ethylate, but by analogy with the
behaviour of benzoic methyl ester with sodium benzylate, which
gave the same additive product as that obtained by combining
benzoic benzyl ester with sodium methylate, showing that such
combinations could occur,

$$C_6H_5C \begin{cases} ONa \\ OCH_3 \\ OCH_2.C_6H_5 \end{cases}$$
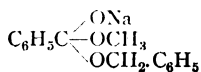
Also by the fact that sodium only attacks ethyl acetate in presence of ethyl alcohol, although the quantity of the latter may be very minute. Similar reactions have been effected with either metallic sodium or sodium ethylate by Claisen, W. Wislicenus and others, of which the following examples must suffice :

$$C_6H_5COOC_2H_5 + CH_3.COOC_2H_5 = C_6H_5CO.CH_2.COOC_2H_5$$
Benzoic ester.   Acetic ester.   Benzoylbenzoic ester. $+ C_2H_5OH.$

$$HCOOC_2H_5 + CH_3.COOC_2H_5 = H.CO.CH_2.COOC_2H_5$$
Formic ester.   Acetic ester.   Formylacetic ester. $+ C_2H_5OH.$

$$C_2H_5OCO.COOC_2H_5 = C_2H_5OCO.CO.CH_2.COOC_2H_5$$
Oxalic ester. $+ CH_3.COOC_2H_5$ Oxalylacetic ester. $+ C_2H_5OH.$
Acetic ester.
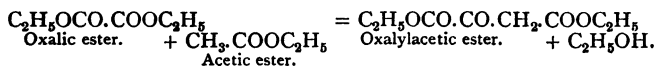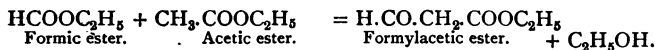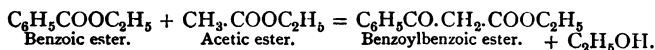
From this it would appear that *condensation* might always be effected between an ester on the one hand and a compound containing the group $CH_2.CO$ on the other. This seems very generally to be the case, and Claisen has succeeded in producing condensation products between esters and ketones or aldehydes containing this group. (See Prep. 87, p. 177.)

The formula for ethyl acetoacetate would imply the properties of a ketone, a view which is borne out by its reduction to an oxy-acid,

$$CH_3.CHOH.CH_2.COOC_2H_5,$$
β-oxybutyric ester.

and by its behaviour with phenylhydrazine and hydroxylamine. The latter reactions give rise to the formation of the usual phenylhydrazone and oxime, whilst a molecule of alcohol is also removed resulting in a closed chain, in the former case phenylmethylpyrazolone, and in the latter methylisoxazolone being formed.

$$CH_3.C.CH_2.CO \qquad\qquad CH_3.C.CH_2.CO$$
$$\|\quad\ |\qquad\qquad\qquad \|\quad\ |$$
$$N\!\!-\!\!-\!\!-\!\!-\!\!N.C_6H_5 \qquad\quad N\!\!-\!\!-\!\!-\!\!-O$$
Phenylmethylpyrazolone.   Methylisoxazolone.
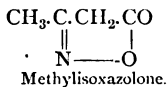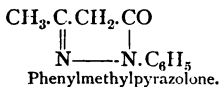
The "methylene" group (CH_2) standing between two CO groups, such as occurs in acetoacetic ester, is characterised by certain properties, which are shared by all compounds of similar structure, viz., by their behaviour towards nitrous acid, diazobenzene salts, and metallic sodium or sodium alcoholate.

The first reaction leads to the formation of isonitrosoacetone,

$$CH_3.CO.CH_2.COOC_2H_5 + HNO_2 = CH_3.CO.CH:NOH + CO_2 + C_2H_5OH.$$

The second yields, in acetic acid solution, *formazyl* derivatives,

$$CH_3.CO.CH_2.COOC_2H_5 + C_6H_5N:N.Cl = CH_3.CO.CH:N.NH.C_6H_5 + CO_2 + C_2H_5OH + HCl.$$

$$CH_3.CO.CH:N.NHC_6H_5 + C_6H_5N:N.Cl$$
$$= CH_3.CO.C \diagup \substack{N:N.C_6H_5 \\ N.NH.C_6H_5} + HCl.$$
Acetyl diphenyl formazyl.

The third is capable of the utmost variety, since the sodium in the sodium compound may be removed by the action of :

1. Iodine, which leads to the formation of acetosuccinic ester,

$$\substack{CH_3.CO.CHNa.COOC_2H_5 \\ + \\ CH_3.CO.CHNa.COOC_2H_5} + I_2 = \substack{CH_3.CO.CH.COOC_2H_5 \\ | \\ CH_3.CO.CH.COOC_2H_5} + 2NaI.$$
Acetosuccinic ester.

2. Alkyl iodide, whereby two atoms of hydrogen may be *successively* replaced by the same or different radicals,

$$CH_3.CO.CHNa.COOC_2H_5 + CH_3I = CH_3.CO.CH(CH_3)COOC_2H_5 + NaI.$$

$$CH_3.CO.CNa(CH_3).COOC_2H_5 + CH_3I = CH_3.CO.C(CH_3)_2.COOC_2H_5 + NaI.$$

3. Acid chloride, which is of similar character to the foregoing process, but gives rise in some cases to the simultaneous formation of two isomeric compounds, a fact which at one time threw considerable doubt on the ketonic character of acetoacetic ester. Thus chloroformic ester and sodium acetoacetic ester produce the following two derivatives :

• $CH_3.CO.CH(CO_2C_2H_5)_2.$ $CH_3.C(OCO_2C_2H_5):CH.CO_2C_2H_5.$
    Acetylmalonic ester.   β-carboxethylacetoacetic ester.

The synthetic capabilities of this compound are not yet exhausted. Acetoacetic ester and its alkyl derivatives undergo decomposition in two ways, according to whether dilute alkalis and acids or, on the other hand, strong alkalis are employed

1. With *dilute* aqueous or alcoholic caustic alkalis, or baryta, or sulphuric acid, a ketone is formed (ketonic decomposition),

$$CH_3.CO.CH_2.COOC_2H_5 + H_2O = CH_3.CO.CH_3. + CO_2 + C_2H_5OII.$$
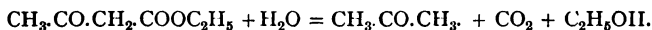
2. Concentrated alcoholic potash decomposes the ester into two molecules of acid (acid decomposition),

$$CH_3.CO.CH_2.COOC_2H_5 + 2II_2O = CH_3.COOH + CH_3.COOH + C_2H_5OH.$$
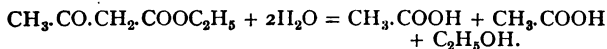
If the alkyl derivatives of the ester are employed, it is possible to effect the synthesis of a series of ketones and saturated aliphatic acids, according to whether the one or other reaction is used.

Of the other synthetic processes which have been studied in connection with this substance, the following may be mentioned :

1. The monoalkyl derivatives yield with nitrous acid the isonitroso derivative, from which the ortho-diketone may be obtained (Pechmann),

$$CH_3.CO.CH(CH_3).COOC_2H_5 + HNO_2 = CH_3.CO.C:(NOH).CH_3 + C_2H_5OH + H_2O.$$

$$CH_3.CO.C:(NOH).CH_3 + H_2O = CH_3.CO.CO.CH_3 + NH_2OH.$$
$$\text{Diacetyl.}$$
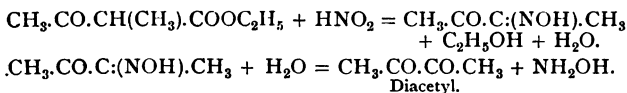
These compounds readily condense, forming derivatives of quinone,

$$\begin{array}{ll} CH_3.C\;\fbox{O}\;.CO.CH\;\fbox{H_2} & CH_3.C.CO.CH \\ HC\;\fbox{H_2}\;.CO.C\;\fbox{O}\;.CH_3 & CH.CO.C.CH_3 \end{array} =$$
$$\text{Dimethyl quinone.}$$
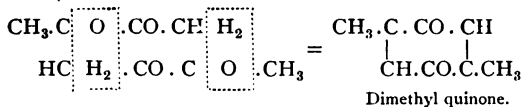
2. Aldehyde-ammonias and acetoacetic ester yield pyridine derivatives (Hantzsch),

Dihydrocollidinedicarboxylic ester.
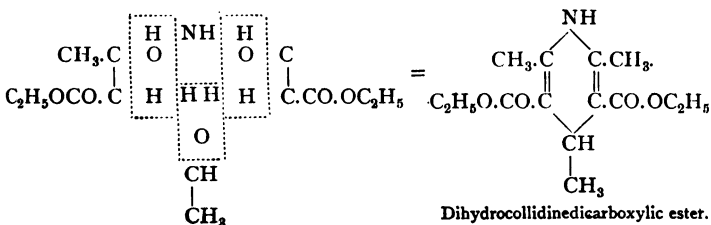
3. Orthoformic ester and acetoacetic ester in presence of acetic anhydride form an oxymethylene ester (Claisen)

$$\begin{array}{l} CH_3 \\ | \\ CO \\ | \\ CH_2 \\ | \\ COOC_2H_5 \end{array} + HC(OOC_2H_5)_3 = \begin{array}{l} CH_3 \\ | \\ CO \\ | \\ C : CH.OC_2H_5 + 2C_2H_5OH. \\ | \\ COOC_2H_5 \end{array}$$
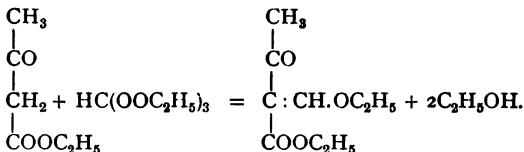
4. The derivatives of acetosuccinic ester are very numerous, the compound lending itself readily to the formation of *heterocylic* ring compounds (pyrrol, furfurane, thiophene, pyridine, &c., derivatives).

The impartial way in which acetoacetic ester was found to behave, sometimes playing the part of a hydroxy-compound, sometimes that of a ketone, has led to much discussion on the merits of the formulæ proposed by Geuther and Frankland,

$$CH_3.C(OH) : CH.COOC_2H_5. \qquad CH_3.CO.CH_2.COOC_2H_5.$$
Geuther's formula.   Frankland's formula.
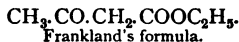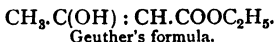
From its physical properties and from its close analogy with compounds which are known in both *desmotropic* forms, there is now little doubt that the liquid is a mixture of both compounds, the proportion of each being determined by temperature and other conditions

PREPARATION 17 AND 18.

Monochloracetic acid and Monobromacetic acid.—The action of chlorine on the aliphatic acids takes place in presence of sunlight, also on the addition of small quantities of the "halogen-carriers," iodine, sulphur, and red phosphorus. By the action of iodine, ICl is formed, which decomposes more readily than the molecule of chlorine, and hydriodic acid is liberated,

$$CH_3.COOH + ICl = CH_2Cl.COOH + HI.$$
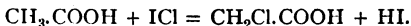
The hydriodic acid is then decomposed by chlorine, and ICl regenerated. Phosphorus acts by forming the chloride of phosphorus from which the acid chloride is produced, which is more readily attacked by chlorine than the acid. Sulphur behaves in a similar fashion, sulphur chloride converting the

acid into the acid chloride. Bromine in presence of phosphorus forms in the same way, first, the acid bromide, and, in the second stage of the reaction, the bromine substitution product. The bromine in all cases attaches itself to the *a*-carbon (*i.e.*, next the carboxyl). Where no free hydrogen exists in this position, as in trimethylacetic acid, no substitution occurs. Iodine can be introduced by the action of KI on the bromine derivative,

$$CH_2Br.COOH + KI = CH_2I.COOH + KBr.$$
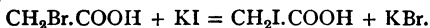
Monohalogen derivatives may also be obtained from the unsaturated acids by the action of the hydracids (HCl, HBr, HI). In this case the halogen attaches itself to the carbon farthest from the carboxyl. Thus acrylic acid gives with HBr the *β* bromopropionic acid,

$$CH_2 : CH\ CO.OH + HBr = CH_2Br.CH_2.COOH.$$

The action of the hydracids, PCl_5 and PBr_5, on the oxy-acids also yields the halogen derivatives,

$$CH_3.CH(OH).COOH + HBr. = CH_3.CHBr.COOH + H_2O.$$
$$CH_3.CH(OH).COOH + 2PCl_5 = CH_3.CHCl.COCl + 2POCl_3 + 2HCl.$$
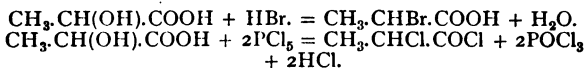
In the latter case the acid chloride must be subsequently decomposed by water to obtain the acid.

The increase in the number of halogen atoms in the acid raises the boiling point as well as the strength of the acid as determined by its dissociation constant K.

	B.P.	K.
Acetic acid	118°	·0018
Monochloracetic acid . . .	185°	·155
Dichloracetic acid	190°	5·14
Trichloracetic acid	195°	121

Some of the transformations of monohalogen acids are illustrated by the following equations :

$$CH_2Cl.COOH + H_2O\ \ = CH_2OH.COOH + HCl.$$
$$CH_2Cl.COOH + KCN\ \ = CH_2CN.COOH + KCl.$$
$$CH_2Cl.COOH + 2NH_3 = CH_2NH_2.COOH + NH_4Cl.$$
$$2CH_2Br.COOH + Ag_2\ \ = \begin{matrix}CH_2.COOH\\ |\\ CH_2.COOH\end{matrix} + 2AgBr$$
$$CH_2I.CH_2COOH + KOH = CH_2 : CH.COOH + KI + H_2O.$$
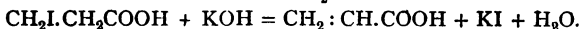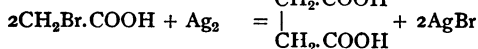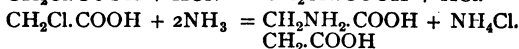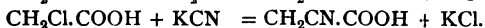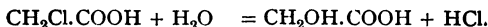
PREPARATION 19.

Glycocoll.— By the action of primary and secondary amines, corresponding amido-acids are formed. Chloracetic acid and methylamine yield sarcosine,

$$CH_2 \diagup{}^{Cl}_{\diagdown COOH} + NH_2CH_3 = CH_2 \diagup{}^{NHCH_3}_{\diagdown COOH} + HCl.$$
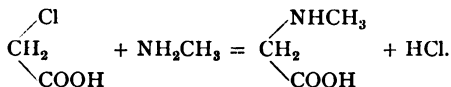
The amido-acids are further obtained by the reduction (Zn and HCl) of nitro-, oximido- and cyano-acids, thus :

$$CH_2(NO_2).COOH + 3H_2 = CH_2(NH_2)COOH + 2H_2O.$$
$$CH_3.C(NOH).COOH + 2H_2 = CH_3.CH(NH_2).COOH + H_2O.$$
$$CN.COOH + 2H_2 = CH_2(NH_2).COOH,$$
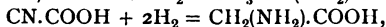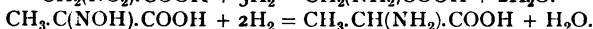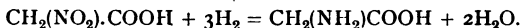
and by the action of NH_3 on the cyanhydrin of aldehydes and ketones, or simply of ammonium cyanide. The product is then hydrolysed with HCl,

$$CH_3.COH \xrightarrow{HCN} CH_3.CH \diagup{}^{CN}_{\diagdown OH} \xrightarrow{NH_3} CH_3.CH \diagup{}^{CN}_{\diagdown NH_2} \xrightarrow{HCl} CH_3.CH \diagup{}^{COOH}_{\diagdown NH_2}$$
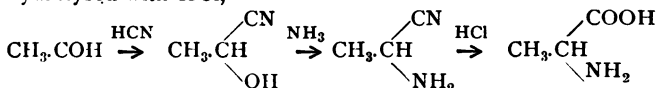
The amido-acids are crystalline compounds usually of a sweet taste and soluble in water. They are neutral compounds, from which it may be assumed that an inner ammonium salt is formed—

$$CH_2 \diagup{}^{NH_3}_{\diagdown COO}$$

By the action of an acid chloride on the amido acid, the hydrogen of the amido group may be replaced by an acid radical. Hippuric acid has been synthesised in this way.

$$CH_2 \diagup{}^{NH_2}_{\diagdown COOH} + C_6H_5COCl = CH_2 \diagup{}^{NH.CO.C_6H_5}_{\diagdown COOH} + HCl.$$
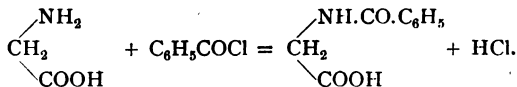
The amido-acids are not acted on by a hot solution of caustic alkali, but on fusion with caustic soda or potash, yield the amine and CO_2

$$CH_3.CH \diagup{}^{NH_2}_{\diagdown COOH} = CH_3.CH_2.NH_2 + CO_2.$$
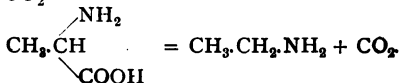
With nitrous acid the oxy-acid is formed,

$$CH_2{<}^{NH_2}_{COOH} + HNO_2 = CH_2{<}^{OH}_{COOH} + N_2 + H_2O.$$
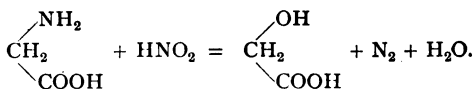
By the action of sodium nitrite in the cold on the hydrochloride of the amido-acid ester, a diazo-ester is formed (Curtius),

$$CH_2{<}^{NH_2HCl}_{COOC_2H_5} + NaNO_2 = CH_2{<}^{N}_{COOC_2H_5} + NaCl + 2H_2O.$$
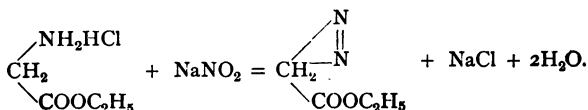
PREPARATION 20.

Diethylmalonate.—In the second part of this preparation, in which HCl is passed into the potassium cyanacetate mixed with alcohol, it should be noted that two reactions occur. The cyanide is hydrolysed to the acid by the action of the hydrochloric acid. At the same time the ester is formed by the action of the hydrochloric acid on the acid and alcohol (see Prep. 32, p. 103).

PREPARATION 21.

Ethylmalonic Acid.—Like acetoacetic ester (see p. 202), diethylmalonate contains the group $CO.CH_2.CO$. By the action of sodium or sodium alcoholate, the hydrogen atoms of the methylene group are successively replaceable by sodium. The sodium atoms are in turn replaceable by alkyl or acyl groups. Thus in the present preparation, ethyl malonic ester is obtained by the action of ethyl iodide on the monosodium compound. If this substance be treated with a second molecule of sodium alcoholate and a second molecule of alkyl iodide, a second radical would be introduced, and a compound formed of the general formula,

$$^X_Y{>}.C(CO_2C_2H_5)_2$$
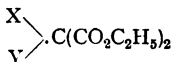
in which X and Y denote the same or different radicals.

These compounds yield, on hydrolysis, the free acids, which like all acids containing two carboxyl groups attached to the

COHEN'S ADV. P. O. C. **P**

same carbon atom, lose CO_2 on heating. Thus, ethyl malonic acid yields butyric acid. In this way the synthesis of mono-basic acids may be readily effected. Malonic ester, moreover, may be used in the preparation of cyclic compounds as well as tetra-basic and also dibasic acids of the malonic acid series (Perkin). To give one illustration : malonic ester and ethylene bromide in presence of sodium alcoholate, yield trimethylene dicarboxylic ester and tetramethylene tetracarboxylic ester. The first reaction takes place in two steps,

$$CHNa(COOC_2H_5)_2 + C_2H_4Br_2 = CH_2Br.CH_2.CH(COOC_2H_5)_2 + NaBr.$$
$$CHNa(COOC_2H_5)_2 + CH_2BrCH_2.CH(COOC_2H_5)$$

$$= \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \!\!> C(COOC_2H_5)_2 + NaBr + CH_2(COOC_2H_5)_2.$$
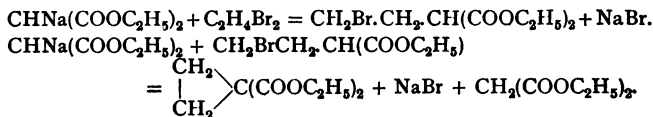
In the second step a second molecule of sodium malonic ester exchanges its sodium with the substituted malonic ester and a second molecule of NaBr is then removed.

The formation of the tetracarboxylic ester occurs simultaneously,

$$2CHNa(COOC_2H_5)_2 + C_2H_4Br_2$$
$$= (COOC_2H_5)_2CH.CH_2.CH_2.CH(COOC_2H_5)_2 + 2NaBr.$$

The free acid derived from the ester by hydrolysis loses two molecules of CO_2, on heating, and gives adipic acid,

$$COOH)_2CH.CH_2.CH_2.CH(COOH)_2$$
$$= COOH.CH_2.CH_2.CH_2.CH_2.COOH + 2CO_2.$$
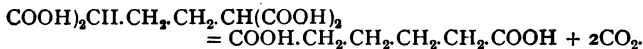
PREPARATION 22.

Trichloracetic Acid.—This acid may also be obtained by direct substitution of acetic acid by chlorine (Dumas) (see Prep. 17, p. 79). The oxidation of the corresponding aldehyde is, however, the more convenient method. Trichloracetic acid decomposes with alkalis on heating into carbon dioxide and chloroform,

$$CCl_3.COOH = CHCl_3 + CO_2.$$
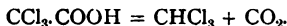
The reaction resembles the formation of methane from sodium acetate, when heated with soda-lime.

On reduction with sodium or potassium amalgam, trichloracetic acid is converted into acetic acid (Melsens),

$$CCl_3.COOH + 3H_2 = CH_3.COOH + 3HCl.$$
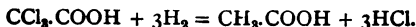
Dichloracetic acid may also be obtained from chloral by the action of potassium cyanide and water,

$$CCl_3COH + H_2O + KCN = CHCl_2.COOH + KCl + HCN.$$
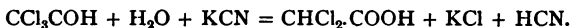
Whereas mono- and trichloracetic acid are solid, dichloracetic acid is a liquid at the ordinary temperature.

PREPARATION 23.

Oxalic Acid.— The preparation of oxalic acid by the action of nitric acid on sugar was introduced by Scheele, and was used for some time as a technical process. The present method is to heat sawdust with a mixture of caustic potash and soda on iron plates to 200-220°, and to lixiviate the product with water. The acid is precipitated as the calcium salt, which is then decomposed with sulphuric acid.

PREPARATION 25.

Palmitic Acid.—This acid, together with stearic and oleic in the form of the glycerides, are the chief constituents of fats. Palmitin (glyceride of palmitic acid) is also found in certain vegetable oils like palm and olive oil. The acid occurs also as the cetyl ester in spermaceti and as the myricyl ester in beeswax. It may be obtained from oleic acid by fusion with potash,

$$C_{18}H_{34}O_2 + 5O + 5KOH = C_{16}H_{31}O_2K + 2K_2CO_3 + 4H_2O.$$

In the analysis of oils and fats, where the quantity of fatty acid is the chief object of the determination, it is customary to hydrolyse the substance with a standard solution of *alcoholic* potash in place of aqueous potash, and to estimate the excess of free alkali with standard acid, using phenolphthalein as indicator. The difference gives the amount of alkali neutralised by the fatty acid.

PREPARATION 26.

Formic Acid.—In addition to the method described, the acid is formed in the decomposition of chloral (see p. 88), chloroform (see Prep. 8, p. 64), by the action of conc. HCl on the isocyanides,

$$C_2H_5NC + H_2O = C_2H_5NH_2 + HCO.OH,$$
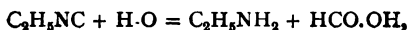
by the decomposition of aqueous hydrocyanic acid, which yields the ammonium salt,

$$HCN + 2H_2O = HCOONH_4,$$
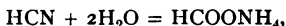
and by the oxidation of methyl alcohol with potassium bichromate, and sulphuric acid. It is present in the sting of ants and nettles, and is also occasionally found among the products of bacterial fermentation of polyhydric alcohols and carbohydrates. The calcium salt is used in the preparation of aldehydes by heating it with the calcium salt of a higher aliphatic acid,

$$(HCOO)_2Ca + (CH_3.COO)_2Ca = 2CH_3CO.H + 2CaCO_3.$$

The reducing action of formic acid and formates on metallic salts may be ascribed to the presence of the aldehyde group $(OH)CH:O$, in the acid.

PREPARATION 27.

Allyl Alcohol.—Note the difference produced by the change in the relative quantities of glycerin and oxalic acid, and the temperature at which the reaction is brought about. In the case of formic acid, it is the oxalic acid alone which undergoes decomposition, and theoretically, a small quantity of glycerin will effect the decomposition of an unlimited amount of oxalic acid. But at the higher temperature it is the glycerin which yields the main product. Allyl alcohol being an unsaturated compound, forms additive compounds with halogens and halogen acids. With permanganate solution it may be converted into glycerin,

$$CH_2:CH.CH_2OH + H_2O + O = CH_2OH.CHOH.CH_2OH.$$
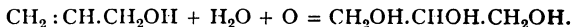
On oxidation with silver oxide it yields the corresponding aldehyde (acrolein) and the acid (acrylic acid).

PREPARATION 28.

Isopropyl Iodide.—The replacement of hydroxyl by iodine in the action of phosphorus and iodine on alcohols has already been described (see Prep. 6, p. 61), but here the presence of an excess of hydriodic acid, which is due to the action of water on the phosphorus iodide,

$$PI_3 + 3H_2O = P(OH)_3 + 3HI,$$
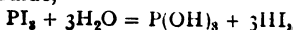
exerts in addition a reducing action on certain of the hydroxyl groups. By diminishing the proportion of phosphorus and iodine to glycerin, the reaction may be interrupted at an earlier stage, when allyl iodide is formed. This is probably due to the splitting off of iodine from propenyl triiodide,

$$CH_2I.CHI.CH_2I = CH_2 : CH.CH_2I + I_2.$$
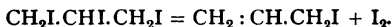
On the other hand a larger proportion of phosphorus and iodine or conc. hydriodic acid will reduce allyl iodide to propylene,

$$CH_2 : CH.CH_2I + HI = CH_2 : CH.CH_3 + I_2.$$
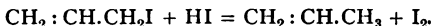
The action of hydriodic acid on glycerin is typical of the polyhydric alcohols. Hydriodic acid converts erythritol into secondary butyl iodide, and mannitol into secondary hexyl iodide. The normal iodides are never formed.

PREPARATION 29.

Epichlorhydrin.—It is a noteworthy fact that although hydrochloric acid can replace hydroxyl by chlorine in the case of the monohydric alcohols, the number of hydroxyl groups which are substituted in the case of polyhydric alcohols is strictly limited. Like glycerin, ethylene glycol gives a chlorhydrin,

$$CH_2OH.CH_2OH + HCl = CH_2OH.CH_2Cl + H_2O.$$
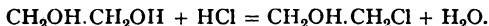
The remaining hydroxyls can always be replaced by chlorine by the action of PCl_5. The chlorhydrins may also be obtained by the action of HOCl on the olefines. It is a general property of these compounds to form the oxide when heated with caustic alkalis. Ethylene chlorhydrin gives ethylene oxide in this way,

$$CH_2Cl.CH_2OH + NaOH = CH_2.CH_2 + NaCl + H_2O.$$
$$\diagdown O \diagup$$
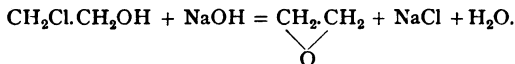
Compounds like ethylene oxide and epichlorhydrin may be regarded as inner ethers,

$$O\diagup\diagdown{CH_2 \atop CH_2} \qquad O\diagup\diagdown{CH_3 \atop CH_3}$$
Ethylene oxide.   Dimethyl ether.
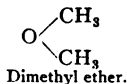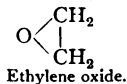
These oxides are easily decomposed. With water, ethylene oxide forms glycol; with hydrochloric acid, the chlorhydrin; with hydrocyanic acid, the cyanhydrin. Epichlorhydrin behaves similarly.

PREPARATION 30

Glyceric Acid.—This is a simple case of oxidation of a primary alcohol-group to a carboxyl-group. The majority of oxidation products which glycerin should give according to its structure are known ; but they have not been obtained by direct oxidation. Though glyceric acid contains an *asymmetric* carbon atom, it is optically inactive (see Notes on Prep. 32, p. 216).

PREPARATION 31.

Succinic Acid.—Tartaric acid, like malic acid, is converted into succinic acid on reduction with HI, and the relationship of these three acids is thereby established. The constitution of succinic acid itself has been determined by its synthesis from ethylene (Maxwell Simpson). Ethylene unites with bromine, forming ethylene bromide, which yields ethylene cyanide with potassium cyanide. The latter is then hydrolysed.

$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \rightarrow \begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} \rightarrow \begin{matrix} CH_2CN \\ | \\ CH_2CN \end{matrix} \rightarrow \begin{matrix} CH_2.COOH \\ | \\ CH_2.COOH \end{matrix}$$
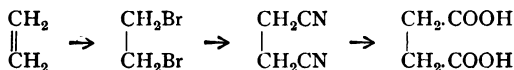
It is an interesting fact, not yet fully explained, that the alkyl succinic acids give anhydrides more readily than succinic acid, and the greater the number of alkyl groups, the more readily is the anhydride produced. Thus the anhydride of tetramethyl succinic acid is so stable that it is not decomposed by water.

The symmetrical dialkyl succinic acids exist in two forms, each yielding a separate anhydride. From their similarity to the anhydrides of hexahydrophthalic acid, they are distinguished as cis- and trans- compounds (see Notes on Prep. 34, p. 218).

Dimethylsuccinic anhydride.   Hexahydrophthalic anhydride.
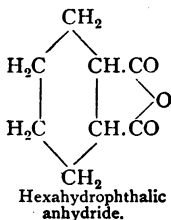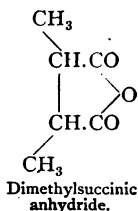
PREPARATION 32.

Ethyl Tartrate.—The speculations of Pasteur (1860) on the cause of the optical activity and hemihedry of tartaric acid and its salts, and of Wislicenus (1873) on the existence of three lactic acids; have developed in the hands of Van't Hoff and Le Bel (1874) into the present theory of stereo-chemistry or atomic space arrangement. Optical activity is found to be invariably associated with the presence in the substance of an *asymmetric* carbon atom, *i.e.* one linked to four different groups. Now every asymmetric (unsymmetrical) object like a hand or foot has its fellow ; but the two do not precisely overlap, and every substance containing an asymmetric carbon atom, round which the four groups are distributed, not, as usually represented, in one plane, but in space of three dimensions, is capable of existing in two forms, which correspond to a left and right hand, or to an object and its reflected image.

This is represented by making the carbon atom the centre of
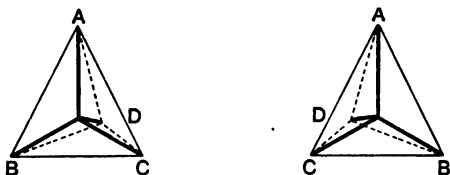
a tetrahedron and attaching the four different groups to the four solid angles. The two forms will then appear as in the Fig. in which ABCD represent four different groups. When using actual models, it will be found that they cannot be turned so as to coincide until two of the groups in one model have been interchanged.

The main difference between two such substances lies in their action on polarized light, the one turning it to the right (dextro-rotatory) and the other to the left (laevo-rotatory), when in the liquid or dissolved state. Although every optically active substance contains at least one asymmetric carbon atom like amyl

alcohol and malic acid, or two like tartaric acid (the asymmetric carbon is represented in heavy type),

$$
\begin{array}{ccc}
CH_3 & CH_2.COOH & H \\
| & | & | \\
C_2H_5—C—H & HO—C—H & HO—C—COOH \\
| & | & | \\
CH_2OH & COOH & HO—C—COOH \\
& & | \\
& & H
\end{array}
$$
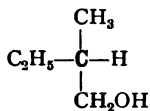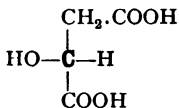
Active amyl alcohol.   Malic acid.   Tartaric acid.
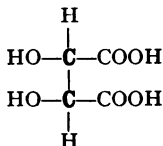
the converse does not always hold ; for there are many compounds which possess an asymmetric carbon atom and show no rotation.   The cause of this may be, either that the substance is a mixture of equal quantities of the two forms, which by having opposite rotations neutralise each other's effect as in the case of racemic acid, which consists of equal quantities of dextro- and laevo- tartaric acid and produces what is termed "external compensation," or the two similar asymmetric carbon atoms exist within the same molecule and neutralise each other's effect by "internal compensation," as in the case of meso-tartaric acid. External compensation is generally exhibited by artificially prepared compounds as distinguished from natural products. Thus glyceric acid from glycerin is inactive, though it contains an asymmetric carbon atom,

$$
\begin{array}{c}
CH_2OH \\
| \\
H—C—OH \\
| \\
COOH
\end{array}
$$
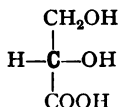
because it consists of a mixture of dextro- and laevo-glyceric acid in equal quantities, whereas tartaric acid, which occurs in grapes, malic acid, which is obtained from mountain ash berries, and also the sugars, terpenes, alcaloids, and a number of other natural products are all active.   One of the great achievements of Pasteur in this line of research was the separation of inactive "externally compensated" compounds into their active components or "optical antipodes."   For further details, a text-book on organic chemistry or stereochemistry must be consulted.

On the formation of ethyl tartrate see Notes on Prep. 15, p. 201. Ethyl tartrate may also be obtained by the method described

in Prep. 86, which rather curtails the operation and does not necessitate the use of more than half the quantity of ethyl alcohol required by the earlier process.

<center>PREPARATION 34.</center>

Citraconic and Mesaconic Acid.—The theory of Le Bel and Van't Hoff has been extended to unsaturated compounds like fumaric and maleic and the above two acids, which form isomeric pairs. These two pairs of acids bear a close resemblance. It has already been observed in the course of the preparation that citraconic is readily converted into mesaconic acid. Moreover they both yield pyrotartaric acid on reduction, but only one, citraconic acid, forms an anhydride. Maleic acid in the same way is easily converted into fumaric acid by bromine, both maleic and fumaric acid yield succinic acid on reduction, but only maleic acid forms an anhydride. The explanation is as follows : In each pair of compounds there exists two carbon atoms linked to one another by a double bond and each attached to two different groups. Van't Hoff refers the isomerism of each pair to a space arrangement, which may be represented by supposing two tetrahedra to be joined by a common edge. As the centre of each tetrahedron is occupied by a carbon atom, and the four bonds are directed towards the four corners of the tetrahedron, this space arrangement will correspond to a doubly-linked carbon. If the two spare corners of each
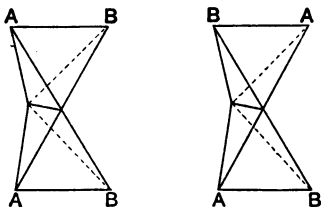
tetrahedron are now occupied by different groups, it is possible to produce two forms by transposing one pair of groups. Supposing A and B to represent two different groups, the above forms will result.

The two pairs of acids will be represented as follows :

| Fumaric acid. | Maleic acid. | Mesaconic acid. | Citraconic acid. |
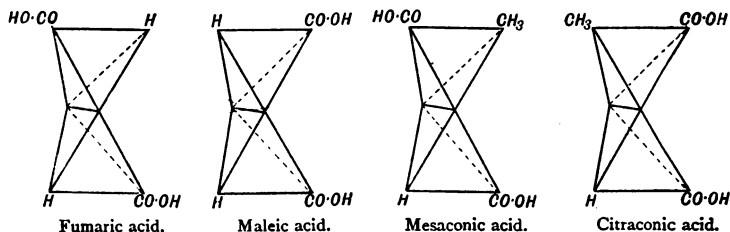
Isomerism in this case is not characterised by optical activity, as the groups lie in one plane and no structural asymmetry is possible. ; but is exhibited by such physical differences as solubility, melting-point, electrical conductivity, and by the fact that in the case of dibasic acids only one of the pair yields an anhydride. Maleic and citraconic acid form anhydrides, but fumaric and mesaconic acid do not. In the case of the acids which form anhydrides, the carboxyl groups are supposed to be nearer together, i.e. on the same side (*cis*) of the molecule, in the other case on opposite sides (*trans*) of the molecule. Maleic and citraconic are " cis " acids, fumaric and mesaconic are " trans " acids. The following table gives the various physical properties, solubility, melting-point, and dissociation constant K of the two pairs of acids.

	S.	M. P.	K.
Maleic	very soluble.	130°	1·17
Fumaric . . .	much less soluble.	sublimes at 200°	·093
Citraconic . . .	very soluble.	80°	·340
Mesaconic . . .	much less soluble.	202°	·079

PREPARATION 35.

Urea.—In addition to the method described in the preparation, urea may be obtained by the oxidation of anhydrous potassium ferrocyanide with potassium bichromate (Williams), or manganese dioxide at a red heat, or by the action of permangante on a cold solution of potassium cyanide (Volhard). It has been synthesised by the action of ammonia on

coffee. The problem has been solved by E. Fischer, who has succeeded in synthesising caffeine in a variety of ways. Fischer found that, by using the same series of processes as described above in the synthesis of uric acid, but substituting dimethyl-alloxan for alloxan, and methylamine sulphite for ammonium sulphite, trimethyl uric acid is formed, and is identical with hydroxycaffeine.

$$CH_3N\text{---}CO$$
$$| \qquad |$$
$$CO \qquad C\text{---}N(CH_3)$$
$$| \qquad \| \qquad \diagdown CO.$$
$$CH_3N\text{---}C\text{---}NH$$

Trimethyl uric acid (Hydroxycaffeine).
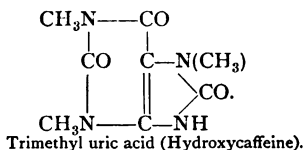
Hydroxycaffeine is converted into caffeine by acting upon it with a mixture of phosphorus pentachloride and oxychloride. This forms chlorocaffeine, which is then reduced with hydriodic acid to caffeine,

$$CH_3N\text{---}CO \qquad\qquad CH_3N\text{---}CO$$
$$| \qquad | \qquad\qquad\qquad | \qquad |$$
$$CO \qquad C\text{---}N(CH_3) \qquad CO \qquad C\text{---}N(CH_3)$$
$$| \qquad \| \qquad \diagdown CCl. \qquad | \qquad \| \qquad \diagdown CH.$$
$$CH_3N\text{---}C\text{---}N \qquad\quad CH_3N\text{---}C\text{---}N$$

Chlorocaffeine.   Caffeine.
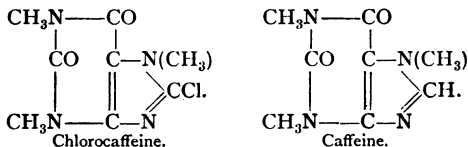
The same result may be obtained in a simpler way by methylating uric acid, and converting it into trimethyluric acid and then into caffeine ; or by preparing the mono- and dimethyl derivatives of uric acid, reducing these to the corresponding mono- and dimethylxanthines and introducing additional methyl groups into the product.

·· PREPARATION 41.

Grape-sugar.—Although grape-sugar yields neither a bi-sulphite compound nor gives Schiff's reaction under ordinary conditions, its properties are for the most part those of an aldehyde. In addition to its reducing action on copper and silver salts, and its combination with phenylhydrazine, it forms an oxime with hydroxylamine and a cyanhydrin with hydro-cyanic acid. On reduction it gives the hexahydric alcohol

sorbitol, and, on oxidation, the corresponding monobasic acid, *gluconic acid*, and the dibasic acid, *saccharic acid*,

$$CH_2OH(CHOH)_4CO.OH. \qquad COOH(CHOH)_4COOH.$$
Gluconic acid. Saccharic acid.
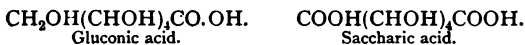
The presence of five hydroxyl groups in glucose is determined by the existence of a pentacetyl derivative. These and other facts, which cannot be discussed in detail, have led to the adoption of the present formula. The discovery of the optical antipode of grape-sugar (which is dextro-rotatory) has determined the present name of dextro-glucose to distinguish it from laevo-glucose, which is laevo-rotatory. For the synthesis of these two sugars and the other mono-saccharoses, a text-book must be consulted.

The other sugars, which reduce alkaline copper sulphate, are fructose (laevulose), galactose, maltose and milk-sugar, the two latter being disaccharoses. They are most readily identified by the microscopic appearance and melting-point of their phenylosazones. Cane-sugar is readily distinguished from the majority of the common sugars by its indifference towards alkaline copper sulphate, until previously boiled with a few drops of dilute sulphuric acid. It is then inverted and gives the reactions for glucose and fructose.

PREPARATION 42.

Bromobenzene.—The replacement of hydrogen by the halogens Cl and Br, in the nucleus of aromatic hydrocarbons, is assisted by the presence of a "halogen carrier," the action of which has been referred to in the Note on the preparations of chlor- and bromacetic acid, p. 206. Iodine, iron, iron and aluminium chlorides and bromides, and the aluminium-mercury couple, all behave in this way. The action of iodine has already been explained on p. 206. Iron and its salts are supposed to act by alternately passing from the ferrous to the ferric state, the ferric salt delivering up its halogen in the nascent state,

$$2FeBr_2 + Br_2 = 2FeBr_3.$$
$$FeBr_3 = FeBr_2 + Br.$$
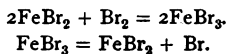
The action of aluminium and its compounds is not fully understood.

Unless a large excess of the hydrocarbon is present, the action of the halogen will effect the substitution of a second atom of hydrogen. By increasing the proportion of halogen, all the hydrogen may be ultimately replaced by chlorine or bromine. Another kind of compound is obtained if the halogen is allowed to act in presence of sunlight. In the case of benzene, the additive compounds, benzene hexachloride and hexabromide, are then formed. They are very unstable compounds, and readily give off hydrochloric and hydrobromic acid. If boiled with alcoholic potash they are decomposed, forming trichloro- and tribromo-benzene,

$$C_6H_6Cl_6 + 3KOH = C_6H_3Cl_3 + 3KCl + 3H_2O.$$

If chlorine and bromine are allowed to act upon an aromatic hydrocarbon like toluene, which has a side-chain, substitution may occur in the nucleus or the side-chain, according to the conditions. Generally speaking, in the cold and in presence of a "halogen carrier," nuclear substitution occurs, but at a high temperature the halogen passes into the side-chain (see Prep. 77, p. 165).

The halogen derivatives of the aromatic hydrocarbons, like those of the aliphatic series, are colourless liquids or solids, denser than water, and possessing an agreeable smell, unless the side-chain is substituted. The latter substances are readily distinguished by their irritating action on the eyes and mucous membrane of the nose (see Prep. 77, p. 165).

The halogen in the aromatic nucleus is much more firmly fixed than in the case of the aliphatic compounds, e.g., bromo-benzene is quite unaffected by most of the reagents which act upon ethyl bromide. The presence of *nitro* groups, however, disturbs this stability, and the halogen in a substance like dinitrochlorobenzene is readily replaced by hydroxyl with potash, or by NH_2 with ammonia. When the halogen is in the side-chain, the substance behaves like an aliphatic compound.

PREPARATION 43.

Ethyl Benzene.—" Fittig's reaction," so-called from its discoverer, is analogous to the synthetical method employed by

Wurtz for the preparation of the aliphatic hydrocarbons, as in the formation of butane from ethyl bromide,

$$2C_2H_5Br + 2Na = C_4H_{10} + 2NaBr.$$
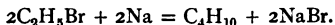
In the case of the aromatic hydrocarbons, a second side-chain may be introduced from a dibromo-derivative either simultaneously with the first, or subsequently by a repetition of the process. Both dibromobenzene and monobromotoluene may be converted into xylene,

$$C_6H_4Br_2 + 2CH_3I + 4Na = C_6H_4(CH_3)_2 + 2NaBr + 2NaI.$$
$$C_6H_4BrCH_3 + CH_3I + 2Na = C_6H_4(CH_3)_2 + NaI + NaBr.$$
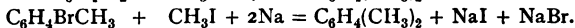
The action also takes place between aromatic hydrocarbons substituted either in the nucleus or side-chain. Bromobenzene yields diphenyl, whereas benzyl bromide yields dibenzyl,

$$2C_6H_5Br + 2Na = C_6H_5.C_6H_5 + 2NaBr.$$
$$2C_6H_5CH_2Br + 2Na = C_6H_5.CH_2.CH_2.C_6H_5 + 2NaBr.$$
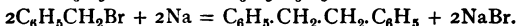
This reaction does not, however, occur with the same readiness in all cases, nor does it always yield exclusively the anticipated product. Para-bromotoluene and sodium give tolyl phenyl methane and dibenzyl as well as ditolyl (Weiler). Occasionally the action is vigorous, and has to be moderated by dilution with an indifferent solvent. At other times it is sluggish and has to be promoted by raising the temperature. Often the addition of a little ethyl acetate will start the decomposition. For the synthesis of some of the aromatic hydrocarbons, it is preferable to use Friedel and Crafts' reaction (see Prep. 89, p. 178).

PREPARATION 44.

Nitrobenzene.—The formation of nitro-compounds, by the action of strong nitric acid on the hydrocarbon, is a distinctive property of aromatic compounds, although recent researches have shown that dilute nitric acid under pressure will convert some of the paraffins, especially the tertiary hydrocarbons, into mono- and dinitro-derivatives. The production of nitro-compounds is usually effected by strong or fuming nitric acid, or solid potassium nitrate, in presence of conc. sulphuric acid. Where the action is vigorous, as in the case of the phenols, it is necessary to use moderately dilute acid. The number of

hydrogen atoms replaceable by the nitro-group (NO_2) is limited. In benzene the first nitro-group is introduced with great ease, the second less readily, and the third with some difficulty. The position taken up by the nitro-groups may be briefly stated as follows : When a negative group (nitro, carboxyl, cyanogen, aldehyde) is already present, the nitro-group enters the meta-position to the first group. In the presence of other groups (alkyl, hydroxyl, halogen, amido), the nitro-group attaches itself to both ortho- and para-positions. Benzoic acid and benz-aldehyde give, on nitration, mainly meta-compounds, whereas toluene, phenol and aniline form simultaneously ortho- and para-derivatives.

Nitro-compounds have often a yellow or red colour, are with difficulty or not at all volatile, possess a much higher boiling-point than the corresponding halogen derivatives, and are denser than water, and insoluble in that liquid.

PREPARATIONS 45—47.

Azoxybenzene, Azobenzene, Hydrazobenzene.—Nitro-compounds yield a series of reduction products according to the nature of the reducing agent. Alkaline reducing agents ; sodium methylate, zinc dust and caustic soda, stannous chloride and caustic soda, produce azoxy-, azo- and hydrazo-compounds,

$C_6H_5NO_2$	C_6H_5N	C_6H_5N	C_6H_5NH
	$>O$	$\parallel$	$\mid$
$C_6H_5NO_2$	C_6H_5N	C_6H_5N	C_6H_5NH
Nitrobenzene.	Azoxybenzene.	Azobenzene.	Hydrazobenzene.
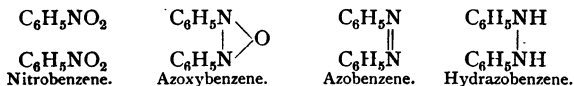
The sodium methylate acts as a reducing agent by taking up oxygen and forming sodium formate.

In the preparations, the nitrobenzene is converted by successive steps into azoxy-, azo- and hydrazo-benzene ; but, by suitably modifying the conditions, the intermediate steps may be omitted. Thus, nitrobenzene may be converted with alcoholic caustic soda and zinc dust directly into hydrazobenzene.

If the reduction of nitrobenzene takes place in neutral solution with zinc dust and water in presence of a little calcium chloride or aluminium-mercury couple and water, β-phenyl hydroxylamine is formed,

$$C_6H_5NO_2 + 2H_2 = C_6H_5NHOH + H_2O.$$
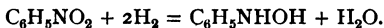
Reduction in acid solution produces an amine (see Prep. 48, p. 129). The reduction of nitrobenzene in alkaline and acid solution has also been effected by electrolysing the liquid in contact with the negative electrode, and excellent yields of azo- and hydrazobenzene (Elbs) and of para-amidophenol (Gattermann) have been obtained in this way. The latter is produced by intramolecular change from phenylhydroxylamine, which is first formed,

$$C_6H_5NHOH = OHC_6H_4NH_2.$$
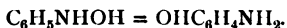
Azobenzene, though not a colouring matter, may be regarded as the mother substance of the large family of azo-colours, which are, however, prepared by a totally distinct method, viz., by the action of a diazo-salt on a phenol or base (see Prep. 66, p. 151). The intramolecular change from hydrazobenzene to benzidine is one of great technical importance. The change occurs by the transfer of the link between the two nitrogen atoms to the two carbon atoms in the *para* position,
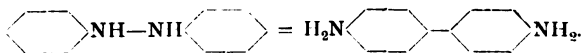
If one of the nuclei of hydrazobenzene is already substituted in the *para* position, the reaction may give rise to diphenylamine derivatives, which are known as ortho- or para-semidines (Jacobson),

Para-semidine.   Ortho-semidine.
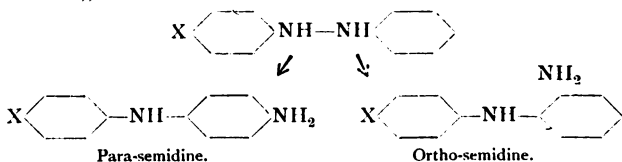
Benzidine and its homologues are used in the manufacture of valuable azo-colours, *congo-red, benzopurpurin* &c. (see p. 239).

Preparation 48.

Aniline.—The reduction of a nitro-compound in an acid solution is a very general method for preparing primary amines. For laboratory purposes it is customary to use tin and hydrochloric or a solution of stannous chloride crystals ($SnCl_2 + 2H_2O$)

in conc. hydrochloric acid or zinc dust and acetic acid. The manufacture of aniline on the industrial scale is effected by means of iron borings and hydrochloric acid ; but of the latter only a fraction of the theoretical quantity, required by the equation $Fe + 2HCl = FeCl_2 + H_2$, is employed. The main reaction is probably represented by the following equation,

$$C_6H_5NO_2 + 2Fe + 4H_2O = C_6H_5NH_2 + Fe_2(OH)_6.$$
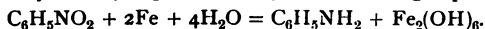
When the base is volatile in steam, as in the present case, the simplest method of separation is to add an excess of alkali and to distil in steam. Otherwise the base may be separated by shaking out with ether, or the tin may be precipitated in the warm solution by H_2S and the filtrate evaporated to dryness. If the compound contains more than one nitro-group, the reduction is carried out with one of the above reducing agents in the manner described, but if it is necessary to reduce only one of the nitro-groups, it is effected by the action of H_2S in presence of ammonia (see Prep. 52, p. 133). Another method, which may also be used for determining the number of nitro-groups, is to prepare an alcoholic solution of the nitro-compound, and to add an alcoholic solution of the calculated quantity of stannous chloride. In this way the reduction of the groups may be carried out in succession and estimated.

The aromatic amines are colourless liquids or solids, which may be distilled without decomposition. Although they form salts with acids, they are much weaker bases than the aliphatic amines owing to the negative character of the phenyl group. The salts have an acid reaction to litmus, whilst the free bases are neutral. The *neutralisation* of an aromatic base by acid is usually determined by the use of methyl violet, magenta, or congo-red paper. The first is turned green, the second colourless, and the third blue by free acid.

Aromatic amines, containing the amido-group in the side-chain, have the basic character and properties of aliphatic amines.

<center>PREPARATIONS 49—50.</center>

Acetanilide, Bromacetanilide.—Primary and secondary bases form acetyl derivatives with acetic acid, acetyl chloride, or acetic anhydride (see Reactions, pp. 68, 69). Tertiary bases are unacted on in this way. As the acetyl

derivatives are much less volatile than the original bases, the method is frequently used for separating a tertiary base from mixtures containing the other two (see Prep. 53, p. 134). The anilides are very stable compounds ; they can be distilled, as a rule, without decomposition, and may be directly brominated, chlorinated, and nitrated. In these reactions, either the ortho- or para- or both derivatives are formed. The remaining hydrogen atom of the amido-group may be replaced by (1) a second acid radical, by the action of acetic anhydride, (2) sodium, by the action of the metal, (3) a nitroso-group, with nitrous acid, and (4) chlorine, by the action of sodium hypochlorite or bleaching powder.

$C_6H_5N(CO.CH_3)_2$	Diacetanilide.
$C_6H_5NNa.CO.CH_3$	Sodium acetanilide.
$C_6H_5N(NO)CO.CH_3$	Nitrosoacetanilide.
$C_6H_5NCl.CO.CH_3$	Acetchloranilide.

All the anilides are hydrolysed by conc. hydrochloric or caustic soda solution and the acid radical removed (see also Beckmann's reaction, Prep. 87, p. 176).

Formanilide is a *tautomeric* compound, *i.e.*, it reacts as though it possessed the alternative formulæ,

$$C_6H_5N : CH(OH) \qquad C_6H_5NH.CO.H,$$

for it yields two isomeric ethers, the one, by the action of methyl iodide on the silver salt, and the other, by the action of methyl iodide on the sodium compound (Comstock). Acetanilide is known in pharmacy as antifebrin, and is used as an antipyretic.

PREPARATIONS 51—52.

Meta-dinitrobenzene.—In the Notes on Prep. 44, p. 224, it is mentioned that the second nitro-group enters the meta-position to the first. This is usually the case where two acid groups are successively introduced into the hydrocarbon. Thus, benzene disulphonic acid, obtained by heating benzene sulphonic acid (see Prep. 67, p. 152) with fuming sulphuric acid, is a meta-compound.

Meta-nitraniline.—The reduction product of meta-dinitrobenzene is naturally meta-nitraniline. The ortho- and para-nitranilines can be obtained by acting upon aniline or, preferably, acetanilide, with fuming nitric acid.

PREPARATION 53.

Dimethylaniline.—It is a well-known fact that the alkyl halides convert the primary amines into secondary and tertiary bases (Hofmann). The formation of dimethylaniline is probably due to the action of CH_3Cl, which is formed, as an intermediate product, by the action of hydrochloric acid on the methyl alcohol. There is always a small quantity of monomethylaniline, $C_6H_5NHCH_3$, produced at the same time. The three bases cannot well be separated by fractional distillation, as their boiling points lie too near together,

$$
\begin{array}{lll}
\text{Aniline} & . \ . \ . \ . \ . \ . \ . \ . \ . \ . & 180°. \\
\text{Methylaniline} & . \ . \ . \ . \ . \ . \ . & 192°. \\
\text{Dimethylaniline} & . \ . \ . \ . \ . & 192°. \\
\end{array}
$$

It is for this reason that the action of acetic anhydride is utilised, which only unites with the primary and secondary base. Dimethylaniline is a weak base, which, like aniline, is neutral to litmus, but gives no stable salts. It is used in the preparation of malachite green (benzaldehyde green) by heating together dimethylaniline, benzaldehyde, and solid zinc chloride. The product (leuco-malachite green) is then oxidised with lead peroxide and hydrochloric acid (see p. 259),

$$
HC\overset{C_6H_5}{\underset{O\ \ H\ |C_6H_4N(CH_3)_2}{\diagdown}} \quad \rightarrow \quad HC\overset{C_6H_5}{\underset{\diagdown C_6H_4N(CH_3)_2}{\overset{\diagup C_6H_4N(CH_3)_2}{\diagup}}}
$$
$$
H\ |C_6H_4N(CH_3)_2
$$

Leuco-malachite green.

$$
\rightarrow \quad HOC\overset{\diagup C_6H_5}{\underset{\diagdown C_6H_4N(CH_3)_2}{\overset{}{-}C_6H_4N(CH_3)_2}}
$$

Base of malachite green.
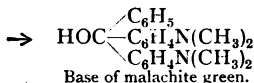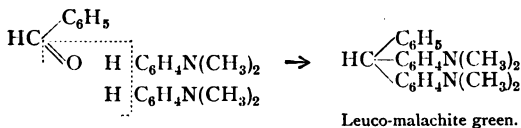
The latter, in presence of the hydrochloric acid, is converted into the hydrochloride,

$$
HOC\overset{\diagup C_6H_5}{\underset{\diagdown C_6H_4N(CH_3)_2}{-C_6H_4N(CH_3)_2}} + HCl = C\overset{\diagup C_6H_5}{\underset{\diagdown C_6H_4:N(CH_3)_2Cl}{-C_6H_4N(CH_3)_2}} + H_2O.
$$

Hydrochloride of
malachite green.
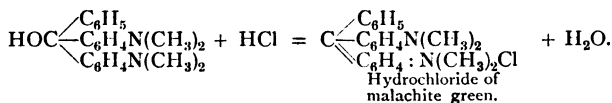
Dimethylaniline is also used for the preparation of tetramethyldiamidobenzophenone (Michler's compound), which forms

the basis of many colouring matters, and is obtained by acting upon dimethylaniline with phosgene (see p. 259),

$$COCl_2 + 2C_6H_5N(CH_3)_2 = OC\begin{smallmatrix} \diagup C_6H_4N(CH_3)_2 \\ \diagdown C_6H_4N(CH_3)_2 \end{smallmatrix} + 2HCl.$$
Michler's compound.
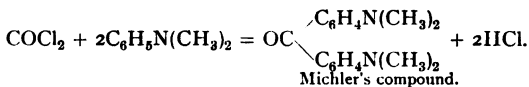
PREPARATION 54.

Nitrosodimethylaniline. — It is a peculiarity of the tertiary aromatic amines, which distinguish them from the corresponding aliphatic compounds, that they are capable of reacting with nitrous acid.   Here the nitroso-group replaces hydrogen in the para-position in the nucleus.

The substances, thus formed, are bases, and form salts with acids, which dissolve in water with a yellow colour.   The solubility of the hydrochloride of the nitroso-bases in water distinguish them from the nitrosamines of the secondary bases, which are insoluble.

Nitrosodimethylaniline is readily oxidised to nitrodimethylaniline.

It is an interesting fact that the nitrosamines of the secondary bases undergo molecular change when acted on with alcoholic hydrochloric acid.   The nitroso-group is thereby transferred to the para-position in the nucleus (E. Fischer),

$$C_6H_5N(NO)CH_3 = NO.C_6H_4.NHCH_3.$$
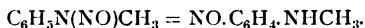
The para-nitroso-derivatives of both secondary and tertiary amines are decomposed with caustic soda into nitrosophenol and alkylamine.

The formation of methylene blue may be explained as follows : By the action of ammonium sulphide on nitrosodimethylaniline, the nitroso-group is reduced to an amido-group.   Two molecules of para-amidodimethylaniline then combine with the elimination of ammonia to form a diphenylamine derivative,

$$(CH_3)_2NC_6H_4 \underset{\cdots\cdots\cdots\cdots}{|\ NH_2 \quad H\ |} HNC_6H_4N(CH_3)_2$$
$$= (CH_3)_2NC_6H_4.NH.C_6H_4.N(CH_3)_2.$$
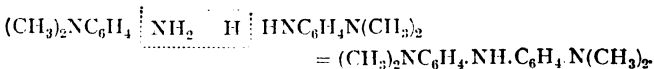
The sulphur of the hydrogen sulphide then enters the mole-

cule under the oxidising influence of the ferric chloride, forming a thiodiphenylamine derivative,

$$(CH_3)_2NC_6H_3—\overset{H}{N}—\overset{O}{\underset{H}{C_6H_3}}.\overset{H}{N(CH_3)_2}Cl$$

$$\begin{matrix} H.—S—H \\ O \qquad O \end{matrix}$$

$$= (CH_3)_2NC_6H_3.N:C_6H_3:N(CH_3)_2Cl.$$
$$\diagdown S\diagup$$

Methylene blue.
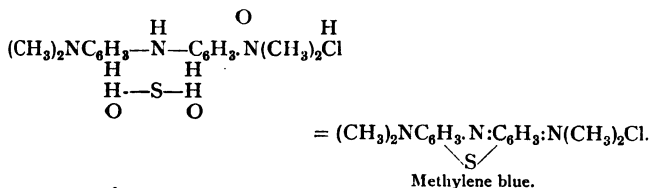
PREPARATION 56.

Phenyl Mustard Oil.—Among the reactions appended to this preparation, the formation of phenyl isocyanate from phenyl mustard oil is described. It should be noted that phenylisocyanate, like the thioisocyanate, unites with ammonia, amines, and more especially with alcohols and phenols.

The bases yield urea derivatives ; the alcohols form urethanes.

$$C_6H_5N:CO + NH_3 = C_6H_5NH.CO.NH_2 \text{ Phenyl urea.}$$
$$C_6H_5N:CO + NH_2CH_3 = C_6H_5NH.CO.NHCH_3 \text{ Methyl phenyl urea.}$$
$$C_6H_5N:CO + C_2H_5OH = C_6H_5NH.CO.OC_2H_5 \text{ Phenyl urethane.}$$
$$C_6H_5N:CO + C_6H_5OH = C_6H_5NH.CO.OC_6H_5 \text{ Phenyl carbamic}$$
phenyl ester.
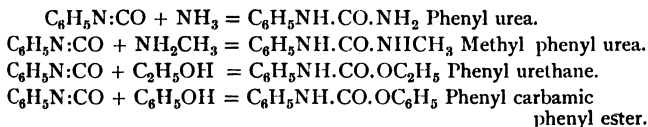
The latter two reactions are frequently used for detecting the presence of a hydroxyl group (Goldschmidt).

PREPARATION 57.

Diazobenzene Sulphate.—Whereas nitrous acid immediately decomposes the primary aliphatic amines with evolution of nitrogen,

$$CH_3NH_2 + HNO_2 = CH_3OH + N_2 + H_2O,$$
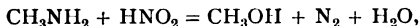
no nitrogen is evolved if nitrous acid is allowed to act upon a salt of a primary aromatic amine *in the cold.* The solution then contains a diazo-salt, which is readily soluble in water. It may already have been observed that in the salts of diazobenzene, the radical, diazobenzene, $C_6H_5N:N.$, plays the part of ammonium, NH_4, in the ammonium salts. Diazobenzene

chloride, nitrate, sulphate, &c., correspond to ammonium chloride, nitrate, and sulphate.

$$C_6H_5N:N.Cl \qquad\qquad NH_4.Cl.$$
$$C_6H_5N:N.NO_3 \qquad\qquad NH_4.NO_3.$$
$$C_6H_5N:N.SO_4H \qquad\qquad NH_4.SO_4H.$$

The hydrate of diazobenzene, $C_6H_5N:N.OH$, which would be analogous to NH_4OH, is also known as an unstable oil. Considerations of this kind have suggested the alternative formula,

$$C_6H_5.N≡N$$
$$|$$
$$X$$
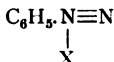
in which X stands for the acid radical (Blomstrand). The nitrogen which combines with the acid radical is thereby penta-valent, as in the ammonium salts. On the other hand, diazo-benzene hydrate forms two isomeric potassium salts, one of which is obtained by adding caustic potash to diazobenzene chloride. This compound is unstable, and unites in the ordi-nary way with phenols to form oxyazobenzene derivatives (see Reaction 5, p. 141). The second one, which is obtained by heating the first to 130° with caustic potash, is very stable, and does not combine directly with phenols (Schraube and Schmidt). Other derivatives of diazobenzene exist in two forms, such as the cyanide and sulphite. The difference has been explained in two ways. According to one theory, the two potassium compounds represent two different space configurations similar to that of citraconic and mesaconic acid (see p. 217) and the oximes (see p. 256), and are distinguished by the terms 'syn' and 'anti' (Hantzsch).

$$C_6H_5N \qquad\qquad\qquad C_6H_5N$$
$$\| \qquad\qquad\qquad\qquad \|$$
$$KO.N \qquad\qquad\qquad\qquad N.OK$$

   Syn-benzene diazotate of potassium.   Anti-benzene diazotate of potassium.
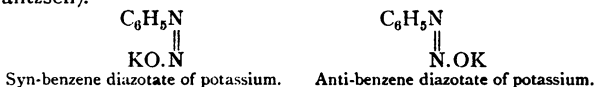
The second theory ascribes the difference to structural arrangement, and the compounds are termed diazo- and isodiazo-compounds (Bamberger).

$$C_6H_5N:NOK. \qquad\qquad C_6H_5NK.NO.$$

   Benzene diazotate of potassium.   Benzene isodiazotate of potassium.

A few of the numerous changes, which the diazo-salts undergo, are illustrated in the series of reactions which follow the prepa-

ration, and are among the most important in organic chemistry. Some of these reactions are carried out on a larger scale in Preps. 58—62. It will there be noticed that it is unnecessary, as a rule, to isolate the diazo-salt, but that the substance is prepared in solution, and is decomposed by the specific reagent.

With few exceptions, all aromatic compounds which contain a nuclear amido- (NH_2) group may be diazotised.

PREPARATION 58.

Para-cresol.—This reaction resembles that of nitrous acid on an aliphatic primary amine ; but the liquid requires to be warmed.

PREPARATION 59.

Para-chlorotoluene.—The action of cuprous chloride, bromide, and cyanide on diazo-chlorides was discovered by Sandmeyer, and is known as 'Sandmeyer's reaction.'

$$C_6H_5N:N.Cl = C_6H_5Cl + N_2.$$
$$C_6H_5N:N.Br = C_6H_5Br + N_2.$$
$$C_6H_5N:N.CN = C_6H_5CN + N_2.$$
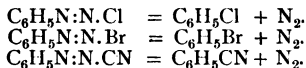
Some of the cuprous chloride compounds of the diazo-salts have been isolated and analysed, and correspond to the formula $C_6H_5N_2Cl.Cu_2Cl_2$ (Hantzsch). The formation of a crystalline copper compound is rendered very evident in the present preparation. A modification of Sandmeyer's reaction is the introduction of precipitated metallic copper in place of the cuprous salt (Gattermann).

The preparation of potassium iodide starch-paper is made by dipping strips of filter paper into a thin solution of starch paste to which a little potassium iodide has been added, and drying the paper.

PREPARATION 60.

Para-iodobenzoic acid.—The oxidation of a side-chain by means of permanganate solution is one which is commonly employed where the acid is required. The monohalogen derivatives are readily oxidised in this way, but greater difficulty is experienced if two halogen atoms are present. The dichlorotoluenes, for example, are only slowly attacked.

Iodosotoluene.—The most interesting of the compounds

belonging to this group, which were so carefully investigated by V. Meyer, is the substance prepared by shaking a mixture of iodosobenzene and iodoxybenzene (obtaine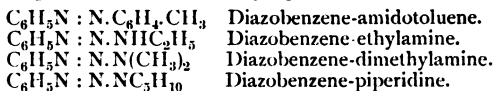d by the oxidation of the iodoso-compound) with moist silver oxide.   Diphenyl-iodonium oxide is thus produced, which in basic properties resembles ammonium hydrate,

$$C_6H_5IO + C_6H_5IO_2 + AgOH = (C_6H_5)_2I.OH + AgIO_3.$$

With hydriodic acid it forms the iodide $(C_6H_5)_2I.I$.

PREPARATION 62.

Diazoamidobenzene.—Diazoamido-compounds are also formed by the action of diazo-salts on primary and secondary amines of both the aliphatic and aromatic series.   The method given in the preparation must then be modified.   The diazo-salt is first prepared, and the amine stirred in with the addition of sodium acetate.   The sodium combines with the mineral acid, liberating the weaker acetic acid, which thereby assists the separation of the diazoamido-compound.   Compounds of the following formulæ have been prepared in this way.

$C_6H_5N : N.C_6H_4.CH_3$ Diazobenzene-amidotoluene.
$C_6H_5N : N.NHC_2H_5$ Diazobenzene-ethylamine.
$C_6H_5N : N.N(CH_3)_2$ Diazobenzene-dimethylamine.
$C_6H_5N : N.NC_5H_{10}$ Diazobenzene-piperidine.

The last compound has been utilised for the preparation of fluorobenzene, and its congeners by the action of conc. hydro-fluoric acid,

$$C_6H_5N : N.C_5H_{10} + 2HF = C_6H_5F + N_2 + C_5H_{10}NH.HF.$$

Diazoamidobenzene undergoes the following reactions :—

1. The hydrogen of the imido-group may be replaced by acid and alkyl radicals.   In the latter case the sodium compound is treated with an alkyl iodide.

2. Phenylisocyanate forms a urea derivative,

$$C_6H_5N : N.NHC_6H_5 + C_6H_5N.CO = C_6H_5N : N.NC_6H_5$$
$$\underset{C_6H_5NH}{\Large{>}}CO.$$
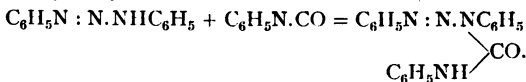
3 With strong hydrochloric acid, decomposition into diazo-salt and amine takes place,

$$C_6H_5N : N.NHC_6H_5 + HCl = C_6H_5N : N.Cl + C_6H_5NH_2.$$
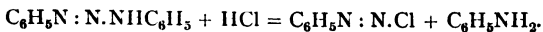
If nitrous acid is added, the second molecule of base is also converted into diazobenzene chloride. In presence of cuprous chloride, chlorobenzene is formed.

4. On boiling with water, diazoamidobenzene decomposes into phenol and base,

$$C_6H_5N : N.NH.C_6H_5 + H_2O = C_6H_5OH + C_6H_5NH_2 + N_2.$$

5. On reduction, it splits up into phenylhydrazine and aniline,

$$C_6H_5N : N.NHC_6H_5 + 2H_2 = C_6H_5NH.NH_2 + C_6H_5NH_2.$$

PREPARATION 63.

Amidoazobenzene.—The conversion of diazoamidobenzene into amidoazobenzene resembles the formation of benzidine from hydrazobenzene (see Reaction 2, p. 129). The diazo-nitrogen seizes on the carbon of the nucleus in the para-position to the amido-group,

$$\bigcirc -N : N.NH\bigcirc = \bigcirc -N : N-\bigcirc NH_2.$$
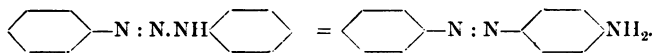
If the para-position is already occupied, the nitrogen takes the ortho-position to the amido-group,

$$\bigcirc -N : N.NH\bigcirc X = \bigcirc -N : N-\bigcirc X \\ NH_2$$

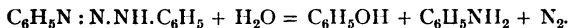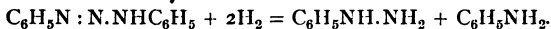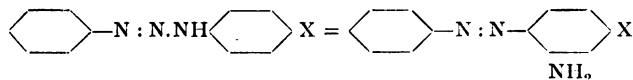but the reaction only takes place readily where the para-position is free. The manner in which the change is brought about has not been satisfactorily explained, although, from the fact that p-diazo-amidotoluene yields, on warming with aniline hydrochloride, p-toluene azoamidobenzene and p-toluidine,

$$CH_3\bigcirc N : N.NH\bigcirc CH_3 + \bigcirc NH_2$$

$$= CH_3\bigcirc N : N\bigcirc NH_2 + CH_3\bigcirc NH_2,$$
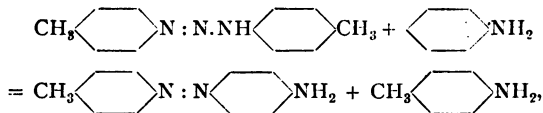
it would appear as if the hydrochloride of the base were the chief factor in the decomposition, and that the change was rather *inter-* than *intra*-molecular. Amidoazobenzene, under the name of *aniline yellow*, has been used as a colouring matter. Its chief technical application at present is in the manufacture of a class of dark blue colours, known as *indulines*. On reduc-

tion with tin and hydrochloric acid, it decomposes into two molecules of base, aniline and para-phenylenediamine, a reaction which is shared by most of the azo-compounds (see p. 240),

$$C_6H_5N : N.C_6H_4NH_2 = C_6H_5NH_2 + NH_2C_6H_4NH_2.$$

PREPARATION 64.

Phenylhydrazine.—The use of phenylhydrazine or, in some cases, para-bromophenylhydrazine, as a reagent for the detection of aldehydes and ketones, has been illustrated in the reactions on pp. 63, 110, and 120. One of its most important technical uses is in the preparation of antipyrine, in which the product, obtained by the action of phenylhydrazine on ethyl acetoacetate, is acted upon with methyl iodide. The two reactions are represented as follows :--

$$
\begin{array}{l}
CH_3.CO.CH_2.COOC_2H_5 \\
\quad + NH_2.NH.C_6H_5
\end{array}
=
\begin{array}{l}
CH_3.C—CH_2.CO \\
\quad \| \qquad | \\
\quad N———N.C_6H_5
\end{array}
+ H_2O + C_2H_5OH.
$$
Phenyl-methyl-pyrazolone.

$$
\begin{array}{l}
CH_3.C—CH_2.CO \\
\quad \| \qquad | \\
\quad N———N.C_6H_5
\end{array}
+ CH_3I =
\begin{array}{l}
CH_3.C=CH.CO \\
\quad | \qquad | \\
CH_3 N———NC_6H_5
\end{array}
+ HI
$$
Phenyl-dimethyl-pyrazolone.
(antipyrine).

The variety of syntheses into which phenylhydrazine enters cannot be described here ; but reference must be made to the text-book.

It should be noted that the action of phenylhydrazine on the ketone group, and of diazobenzene salts on the methylene group situated between two CO groups, are analogous to that of hydroxylamine and nitrous acid upon these two groups, of which the following are examples :—

$$
1. \quad
\begin{array}{l}
CO.OC_2H_5 \\
| \\
CO \\
| \\
CO.OC_2H_5
\end{array}
\begin{array}{l}
\nearrow \quad + NH_2.NHC_6H_5 =
\begin{array}{l}
COOC_2H_5 \\
| \\
C:N.NH.C_6H_5 + H_2O \\
| \\
COOC_2H_5
\end{array}
\\
\\
\searrow \quad + NH_2OH \qquad =
\begin{array}{l}
COOC_2H_5 \\
| \\
C : NOH + H_2O \\
| \\
COOC_2H_5
\end{array}
\end{array}
$$
Mesoxalic
ester.

$$
\begin{array}{c}
\text{COOC}_2\text{H}_5 \\
|\\
\text{CH}_2 \\
|\\
\text{COOC}_2\text{H}_5 \\
\text{Succinic} \\
\text{ester.}
\end{array}
$$

2.

$$+ \text{ClN:N.C}_6\text{H}_5 =
\begin{array}{c}
\text{COOC}_2\text{H}_5 \\
|\\
\text{C:N.NH.C}_6\text{H}_5 \\
|\\
\text{COOC}_2\text{H}_5
\end{array}
+ \text{HCl.}
$$

$$+ \text{O:NOH} =
\begin{array}{c}
\text{COOC}_2\text{H}_5 \\
|\\
\text{C:NOH} \\
|\\
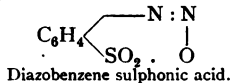\text{COOC}_2\text{H}_5
\end{array}
+ \text{H}_2\text{O}
$$

Phenylhydrazine has been used in the synthesis of indol derivatives. The hydrazones of aldehydes and ketones containing a methyl group are decomposed on heating with zinc chloride, indols being formed with elimination of ammonia. (E. Fischer.)

$$
\begin{array}{c}
\text{CH}_3 \\
|\\
\text{C}_6\text{H}_5\text{NH.N : C} \\
|\\
\text{CH}_3
\end{array}
= \text{C}_6\text{H}_4
\begin{array}{c}
\diagup\text{NH}-\text{C} \\
\diagdown \underset{\text{-----}}{|}\text{CH}
\end{array}
\begin{array}{c}
\text{CH}_3 \\
|\\
 \\

\end{array}
+ \text{NH}_3
$$

Acetone-phenylhydrazone.   Methyl indol.
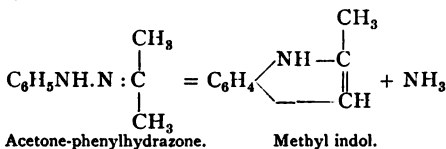
PREPARATION 65.

Sulphanilic Acid.—The acid characters of this substance, which is both base and acid, are more prominently developed than the basic character. Nevertheless, it reacts with nitrous acid like a primary amine, and forms a diazo-salt, which has the following constitution (see Prep. 66, p. 151) :—
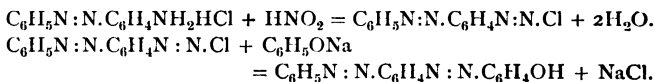
$$
\text{C}_6\text{H}_4
\begin{array}{c}
\diagup\text{----N : N} \\
\diagdown\text{SO}_2 . \text{O}
\end{array}
$$

Diazobenzene sulphonic acid.

The formation of sulphanilic acid is probably preceded by the sulphonation of the amido-group,

$$\text{C}_6\text{H}_5\text{NH.SO}_3\text{H.}$$

A compound of this character has been obtained, which decomposes with acids into ortho- and para-amidosulphonic acid by a process of intramolecular change (Bamberger). The para-compound is exclusively formed at the higher temperature, which may account for the production of this compound in the present preparation.

PREPARATION 66.

Methyl Orange.—The first point to notice in this reaction is that the diazo-salt forms no diazoamido-compound with the dimethylaniline, but at once produces an azo-compound. This is always the case with tertiary amines, some secondary amines like diphenylamine and the phenols. The reaction may be regarded as typical of the formation of all azo-colouring matters. At least two substances are requisite in this process ; on the one hand an aromatic compound containing an amido-group in the nucleus, and, on the other hand, a base or phenol. The first is diazotised and combined or coupled with the second. The coupling takes place, in the case of amines, in a faintly alkaline or neutral solution, in the case of phenols, in an alkaline solution (see Reaction 5, p. 141). In all cases the diazo-group seizes upon the carbon in the para-position to the amido- or hydroxyl group of the coupled nucleus. When the para-position is already appropriated, the ortho-position serves as the link, but no coupling ever occurs in the meta-position. The sulphonic acid derivatives of the base or phenol are frequently preferable to the unsubstituted compound. The dyes formed have, in consequence of the presence of the SO_3H group, an acid character, which renders them capable of forming soluble sodium salts, and adapts them better for dyeing purposes. When an azo-compound is formed by coupling the diazo-compound with a primary amine, the new product is capable of being diazotised and coupled a second time. Thus a tetrazo-compound is formed, containing a double diazo-group $-N:N-$. Amidoazobenzene, when diazotised, forms diazo-azobenzene with nitrous acid, which, like a simple diazo-compound, reacts with the phenols,

$$C_6H_5N:N.C_6H_4NH_2HCl + HNO_2 = C_6H_5N:N.C_6H_4N:N.Cl + 2H_2O.$$
$$C_6H_5N:N.C_6H_4N:N.Cl + C_6H_5ONa$$
$$= C_6H_5N:N.C_6H_4N:N.C_6H_4OH + NaCl.$$

If sulphanilic acid is diazotised and coupled with a second molecule of sulphanilic acid, and then the product again diazotised and coupled with β-naphthol, *Biebrich scarlet* is formed,

$$C_6H_4{<}^{SO_3H}_{N:N.C_6H_3{<}^{SO_3H}_{N:N.C_{10}H_6OH.}}$$

Biebrich scarlet.
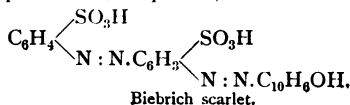
if in the last phase the different sulphonic acids of β-naphthol are employed, various shades of red, known as *Croceins*, are produced. Thus it appears that the colour deepens from orange to red with the introduction of a second azo-group.

This is not the only method of forming tetrazo-compounds. Each amido-group of a diamine may be diazotised and coupled. Benzidine and its homologues, which have been utilised in this way, have a special value for the cotton dyer, as the shades produced are not only very brilliant, but, unlike the majority of colouring matters, are *substantive colours, i.e.*, possess the property of attaching themselves to the cotton fibre without the aid of a mordant. *Congo reds* and *benzopurpurins* are combinations of benzidine and its homologues with the sulphonic acids of naphthol and naphthylamine. The following is the constitution of Congo red, the simplest of these compounds, which is used in the form of its sodium salt :—

$$N : N . C_{10}H_5 \Big\langle {}^{NH_2}_{SO_3Na}$$

$$N : N . C_{10}H_5 \Big\langle {}^{NH_2 \cdot}_{SO_3Na.}$$
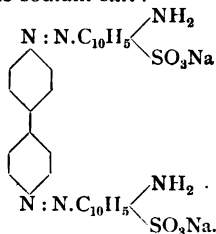
Attention should be drawn to the fact, that azobenzene, although a brightly coloured substance, is without dyeing properties, *i.e.*, it is not a colouring matter, whereas amidoazobenzene and methyl orange are true dyes. They all three contain the azo-group ($-N:N-$), called by Witt a *chromophore*, united to two aromatic nuclei ; but in the case of amidoazobenzene and methyl orange, one of these nuclei contains a basic group, NH_2 or $N(CH_3)_2$. It will also have been observed that the combinations with phenols likewise result in the production of colouring matters. It would appear, therefore, as if there were at least two essentials to a dye, a fundamental or mother substance like azobenzene, termed a *chromogenic* compound, and an amido- or hydroxyl group, called an *auxochrome*. The same thing has been observed in case of other colouring matters (see Note on Prep. 89, p. 257).

Most of the azo-colours split at the double link, on reduction with stannous chloride and hydrochloric acid, forming two molecules of base. Methyl orange yields sulphanilic acid and dimethyl para-phenylenediamine,

$$SO_3H.C_6H_4N : N.C_6H_4N(CH_3)_2 + 2H_2$$
$$= SO_3H.C_6H_4NH_2 + NH_2C_6H_4N(CH_3)_2.$$
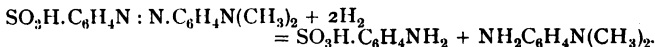
PREPARATION 67.

Potassium Benzene Sulphonate.—The formation of sulphonic acids by the action of sulphuric acid, &c., on the aromatic hydrocarbon is a special property of aromatic hydrocarbons, although, in a few cases, paraffins have been found to react in a similar manner. The process is called "sulphonation." In place of conc. sulphuric acid, fuming sulphuric acid, *i.e.*, an acid containing varying proportions of sulphur trioxide (see Prep. 93, p. 182), and, occasionally, chlorosulphonic acid, $ClSO_2OH$, are used. In the two latter cases sulphones are sometimes formed as a bye-product,

$$2C_6H_6 + SO_3 = (C_6H_5)_2SO_2 + H_2O.$$
$$2C_6H_6 + ClSO_2OH = (C_6H_5)_2SO_2 + HCl + H_2O.$$
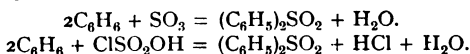
The sulphonic acids are also obtained by the oxidation of thiophenols, a reaction which, at the same time, indicates their constitution,

$$C_6H_5SH + O_3 = C_6H_5SO_3H.$$
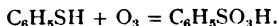
The majority of aromatic sulphonic acids are very soluble in water, and are difficult to obtain in the crystalline form. On the other hand, the sodium or potassium salts generally crystallise well, and it is customary to prepare them by pouring the sulphonic acid directly after sulphonation into a strong solution of sodium or potassium chloride (Gattermann).

The sulphonic acids decompose on heating into the hydrocarbon and SO_3. This reaction is greatly facilitated by heating with conc. hydrochloric acid to 150—180° (Jacobsen), or by passing superheated steam into the sulphonic acid mixed with moderately strong sulphuric acid (Armstrong).

This method is sometimes used for separating hydrocarbons, one of which is more easily sulphonated than another. The sulphonic acid is separated from the unchanged hydrocarbon,
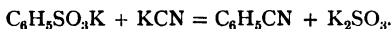
and the hydrocarbon is then regenerated from the sulphonic acid.

The salts of the sulphonic acids undergo the following reactions :—

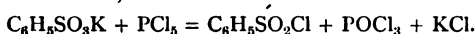1. By fusion with caustic alkalis, phenols are prepared (see Preps. 69, 91 and 94),

$$C_6H_5SO_3Na + NaOH = C_6H_5OH + Na_2SO_3.$$
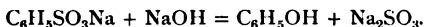
2. By distillation with potassium cyanide, the nitriles are obtained,

$$C_6H_5SO_3K + KCN = C_6H_5CN + K_2SO_3.$$

3. By fusion with sodium formate, the sulphonic group is replaced by carboxyl,

$$C_6H_5SO_3Na + HCOONa = C_6H_5COONa + NaHSO_3.$$
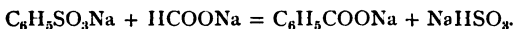
4. By the action of phosphorus pentachloride the sulphonic chloride is obtained,

$$C_6H_5SO_3K + PCl_5 = C_6H_5SO_2Cl + POCl_3 + KCl.$$

PREPARATION 68.

Benzenesulphonic Chloride.—The sulphonic chlorides differ from the carboxylic chlorides in being very slowly decomposed by water. They react, however, in an analogous fashion with alcohols, phenols, and amines in presence of caustic soda.

The behaviour of primary, secondary, and tertiary amines has been suggested as a basis of separation of these three classes of compounds. The primary amines usually form compounds with the sulphonic chloride, which dissolve in caustic soda ; the derivatives of the secondary amine are insoluble, whereas the tertiary amines do not react with the sulphonic chloride (Hinsberg). The method cannot always be employed.

On reduction of the sulphonic chloride with zinc dust and water, the zinc salt of the sulphinic acid is formed,

$$2C_6H_5SO_2Cl + 2Zn = (C_6H_5SO_2)_2Zn + ZnCl_2.$$
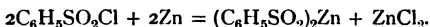
The acid is separated from the zinc salt by boiling with sodium carbonate, filtering from zinc carbonate, and decomposing the soluble sodium salt with sulphuric acid, which precipitates the sulphinic acid.

The sulphinic acids are unstable compounds. They are readily

oxidised to sulphonic acids ; on fusion with alkalis they are con-
verted into the hydrocarbon and alkaline sulphite,

$$C_6H_5.SO_2Na + NaOH = Na_2SO_3 + C_6H_6$$

on reduction they form thiophenols,

$$C_6H_5.SO_2H + 2H_2 = C_6H_5SH + 2H_2O.$$
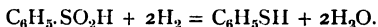
PREPARATION 69.

Phenol.—Fusion of the alkaline salt of the sulphonic acid
with caustic soda or potash is a common method for preparing
phenols (see Preps. 91 and 94). They correspond in consti-
tution to the tertiary alcohols of the aliphatic series, but differ
in their more negative character. The phenols dissolve in
caustic alkalis, forming alkaline phenates, which are, however,
decomposed by carbon dioxide. In this way a phenol may be
separated from an acid. The solution in caustic soda is satu-
rated with carbon dioxide, and the phenol is then extracted
with ether or filtered off. The entrance of nitro-groups into
the nucleus converts phenols into strong acids (see Preps. 71
and 72).

The various reactions which the phenols undergo are illus-
trated in Preps. 71, 72, 73, 74, and 75.

The technical method for obtaining phenol is by shaking out
with caustic soda the " middle oil " of the coal-tar distillate, after
some of the naphthalene has crystallised out. The phenol dis-
solves in the alkali, and is then removed from insoluble oils.
The alkaline liquid is acidified, the phenol separated, distilled,
and finally purified by freezing.

PREPARATION 70.

Anisol.—The preparation of anisol from phenol is analogous
to Williamson's synthesis of the ethers (see p. 190), but the
ethers of phenol cannot be obtained by the action of the alcohol
on the phenol in presence of sulphuric acid. This reaction can,
however, be effected in the case of the naphthols (see p. 260).

The methyl group in anisol can be split off, and the phenol
regenerated by heating with HCl or HI,

$$C_6H_5OCH_3 + HI = CH_3I + C_6H_5OH.$$
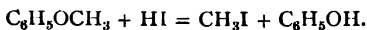
The latter reaction has been made the basis of a quantitative method for determining the number of methoxyl groups (OCH_3) present in a compound. The compound is warmed with conc. hydriodic acid, and, after removing free hydriodic acid, the methyl iodide vapour is passed into an alcoholic solution of silver nitrate, which decomposes the iodide, precipitating silver iodide. The silver iodide is then weighed (Zeisel).
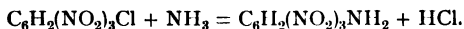
PREPARATION 71.

Ortho- and Para-nitrophenol.—The action of nitric acid on phenol is much more energetic than it is in the case of benzene. To obtain the mono-derivatives, the acid has, in consequence, to be diluted.

The entrance of the nitro-group renders the phenol more strongly acid, so that the nitrophenols, unlike the phenols, form stable salts with alkaline carbonates. It should be noted that the nitro-group enters the ortho- and para-position, but not the meta-position to the OH group, according to the general rule explained on p. 225. Moreover, the ortho-compound is more volatile than the para-compound. Compare ortho- and para-oxybenzaldehyde (Prep. 74, p. 159).

PREPARATION 72.

Picric Acid.—The presence of three nitro-groups converts the phenol into a strong acid. Picryl chloride, which is formed by the action of PCl_5 on the acid, behaves like an acid chloride, is decomposed by water and alkalis, and forms picramide or trinitraniline with ammonia,
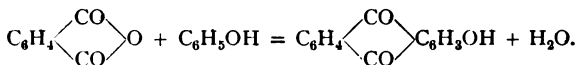
$$C_6H_2(NO_2)_3Cl + NH_3 = C_6H_2(NO_2)_3NH_2 + HCl.$$

Note that the three nitro-groups occupy meta-positions in regard to one another; ortho- or para-positions in reference to the hydroxyl group.
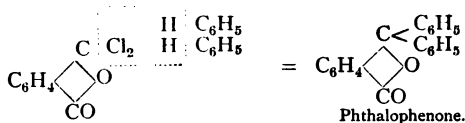
PREPARATION 73.

Phenolphthalein.—The action of phthalic anhydride on phenol takes place in two ways. When equal molecules of the
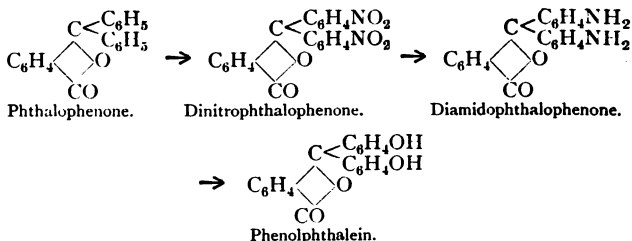
substance react in presence of conc. sulphuric acid, oxyanthra-
quinone is formed (Baeyer),

$$C_6H_4\underset{CO}{\overset{CO}{\diagdown\hspace{-0.3em}\diagup}}O + C_6H_5OH = C_6H_4\underset{CO}{\overset{CO}{\diagdown\hspace{-0.3em}\diagup}}C_6H_3OH + H_2O.$$
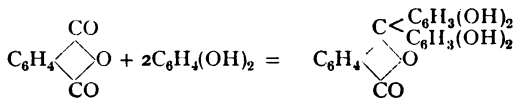
It is by a similar process that alizarin has been synthesised
with the object of ascertaining its constitution (see Notes on
Prep. 94, p. 261). When two molecules of phenol and one mole-
cule of phthalic anhydride are heated together with conc. sul-
phuric acid, then phenolphthalein is formed (Baeyer). Its
constitution has been determined by its synthesis from phthalyl
chloride and benzene by means of " Friedel and Crafts' reaction "
(see Notes on Prep. 87, p. 254). Phthalyl chloride and benzene
yield in presence of AlCl$_3$ phthalophenone,

$$C_6H_4\underset{CO}{\overset{C\ Cl_2}{\diagdown\hspace{-0.3em}\diagup}}O \quad \overset{H\ |\ C_6H_5}{\underset{H\ |\ C_6H_5}{}} = C_6H_4\underset{CO}{\overset{C<\substack{C_6H_5\\C_6H_5}}{\diagdown\hspace{-0.3em}\diagup}}O$$

Phthalophenone.

Phthalophenone is then converted successively into dinitro-
diamido-, and, finally, by the action of nitrous acid, into dioxy-
phthalophenone or phenolphthalein,

$$C_6H_4\underset{CO}{\overset{C<\substack{C_6H_5\\C_6H_5}}{\diagdown\hspace{-0.3em}\diagup}}O \rightarrow C_6H_4\underset{CO}{\overset{C<\substack{C_6H_4NO_2\\C_6H_4NO_2}}{\diagdown\hspace{-0.3em}\diagup}}O \rightarrow C_6H_4\underset{CO}{\overset{C<\substack{C_6H_4NH_2\\C_6H_4NH_2}}{\diagdown\hspace{-0.3em}\diagup}}O$$

Phthalophenone.   Dinitrophthalophenone.   Diamidophthalophenone.

$$\rightarrow C_6H_4\underset{CO}{\overset{C<\substack{C_6H_4OH\\C_6H_4OH}}{\diagdown\hspace{-0.3em}\diagup}}O$$
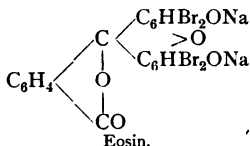
Phenolphthalein.

A more important substance than phenolphthalein is fluor-
escein, which is obtained by heating together phthalic anhydride
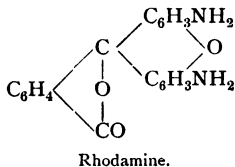and resorcinol, and has a similar constitution,

$$C_6H_4\underset{CO}{\overset{CO}{\diagdown\hspace{-0.3em}\diagup}}O + 2C_6H_4(OH)_2 = C_6H_4\underset{CO}{\overset{C<\substack{C_6H_3(OH)_2\\C_6H_3(OH)_2}}{\diagdown\hspace{-0.3em}\diagup}}O$$

At the same time, the tetroxy-compound loses water and forms fluorescein,

$$C_6H_4 \Big< \begin{matrix} C < \begin{matrix} C_6H_3(OH) \\ >O \\ C_6H_3(OH) \end{matrix} \\ | \\ O \\ | \\ CO \end{matrix}$$
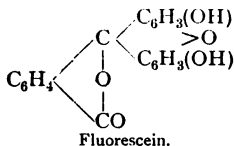
Fluorescein.

By the action of the halogens on fluorescein, dissolved in acetic acid or alcohol, the eosins are obtained, colouring matters which are characterised, like fluorescein, by their fluorescence in alkaline or alcoholic solution, but possess a red instead of a green colour (Caro). The formula for the sodium salt of tetra-bromofluorescein or ordinary eosin is represented thus :

$$C_6H_4 \Big< \begin{matrix} C < \begin{matrix} C_6HBr_2ONa \\ >O \\ C_6HBr_2ONa \end{matrix} \\ | \\ O \\ | \\ CO \end{matrix}$$

Eosin.

An important group of colouring matters, known as the "rhodamines," is obtained from phthalic anhydride and meta-amidophenol and its derivatives. They have a constitution similar to that of fluorescein. The simplest of these compounds is represented by the following formula :—

$$C_6H_4 \Big< \begin{matrix} C < \begin{matrix} C_6H_3NH_2 \\ \\ >O \\ C_6H_3NH_2 \end{matrix} \\ | \\ O \\ | \\ CO \end{matrix}$$

Rhodamine.

PREPARATION 74.

Salicylaldehyde, Para-oxybenzaldehyde.—" Reimer's reaction " for the preparation of oxyaldehydes from phenols is applicable to a very large number of monohydric and polyhydric phenols. The substitution of two H atoms by two aldehyde groups sometimes occurs, as in the case of resorcinol. An

analogous reaction is that of caustic potash and carbon tetra-chloride on phenol, which yields chiefly para-oxybenzoic acid,
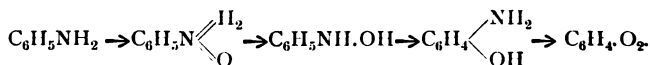
$$C_6H_5OH + CCl_4 + 5KOH = C_6H_4\begin{smallmatrix}OH\\COOK\end{smallmatrix} + 4KCl + 3H_2O.$$
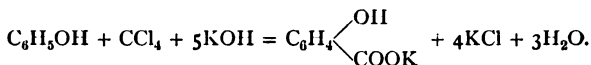
PREPARATION 75.

Salicylic Acid.—The reaction was discovered by Kolbe, and is known as " Kolbe's synthesis." It will have been observed that it takes place in two steps. Sodium phenylcarbonate is first formed, which then undergoes intramolecular change with the production of sodium salicylate (Schmidt). The technical process is carried out in autoclaves, in which carbon dioxide is passed into the sodium phenate under pressure at 120—130°. It is a curious fact that the use of potassium phenate yields, especially at a high temperature (220°), almost exclusively the para-oxybenzoate of potassium.

The above reaction may be applied in the case of other phenols.

PREPARATION 76.

Quinone and Quinol.—Quinone, which was originally obtained by the oxidation of quinic acid (the acid associated with quinine in cinchona bark), is now prepared from aniline. The aniline, in process of oxidation to quinone, appears to pass through the following intermediate stages,

$$C_6H_5NH_2 \rightarrow C_6H_5N\begin{smallmatrix}H_2\\O\end{smallmatrix} \rightarrow C_6H_5NH.OH \rightarrow C_6H_4\begin{smallmatrix}NH_2\\OH\end{smallmatrix} \rightarrow C_6H_4.O_2.$$
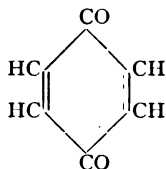
The aniline is first oxidised to phenylammonium oxide, which changes into phenylhydroxylamine. The latter also undergoes intramolecular change, being converted into para-amido phenol, which is finally oxidised to quinone (Bamberger). It may also be obtained by the oxidation of para-derivatives of aniline, such as para-phenylenediamine, sulphanilic acid, para-amidophenol, &c., but it cannot be prepared from an amido-compound or phenol, if an alkyl or carboxyl group occupy the

para-position.   Quinone is sometimes regarded as a superoxide (Graebe), sometimes as a para-diketone (Fittig).
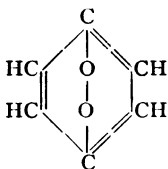

Superoxide formula.   Diketone formula.

The facts in favour of the first are that quinone, like a peroxide, has a strong oxidising action, that on reduction it yields, not a glycol, but a dihydroxybenzene ; moreover, with PCl_5 instead of a tetra-chloro- derivative, a dichlorobenzene is formed.   In favour of the ketone structure is the formation of a mono- and di-oxime (Goldschmidt).
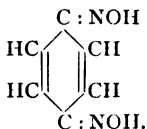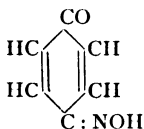
Phenylhydrazones are not formed, as phenylhydrazine acts as a reducing agent and forms quinol.

The constitution of quinhydrone, the intermediate product formed by the reduction of quinone or oxidation of quinol, is represented by the formula,
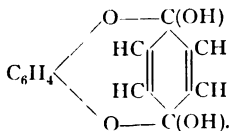
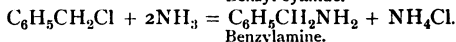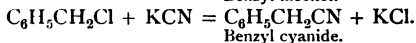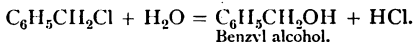·For the formation of dimethylquinone, see p. 205.

PREPARATION 77.

Benzyl Chloride.—The action of chlorine on *boiling* toluene is quite distinct from the action which occurs in the cold or in presence of a " halogen carrier " (see pp. 206, 222). In the present instance substitution takes place in the side-chain.

By prolonged action all three hydrogen atoms of the side-chain may be replaced, and the following compounds obtained :—

$C_6H_5CH_2Cl$ Benzyl chloride.
$C_6H_5CHCl_2$ Benzal chloride.
$C_6H_5CCl_3$ Benzotrichloride.
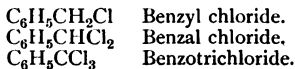
Hydrocarbons containing the halogen in the side-chain may be readily distinguished, by their irritating action on the eyes and mucous membrane of the nose, from those in which the halogen is present in the nucleus. Moreover, the halogen in the side-chain is much more readily substituted or removed than when it occurs in the nucleus. In this respect the above compounds resemble the members of the aliphatic series (alkyl and alkylene halides). Benzyl chloride is decomposed by water, ammonia, and potassium cyanide, forming benzyl alcohol, benzyl cyanide, and benzylamine.

$$C_6H_5CH_2Cl + H_2O = C_6H_5CH_2OH + HCl.$$
Benzyl alcohol.

$$C_6H_5CH_2Cl + KCN = C_6H_5CH_2CN + KCl.$$
Benzyl cyanide.

$$C_6H_5CH_2Cl + 2NH_3 = C_6H_5CH_2NH_2 + NH_4Cl.$$
Benzylamine.

It is also much more easily oxidised than toluene to benzoic acid.

$$C_6H_5CH_2Cl + O_2 = C_6H_5COOH + HCl.$$
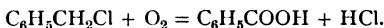
Benzal chloride and benzotrichloride are also decomposed by water, the former in presence of calcium carbonate, and the latter at a high temperature, yielding, in the one case, benzaldehyde, and in the other, benzoic acid.

$$C_6H_5CHCl_2 + H_2O = C_6H_5COH + 2HCl.$$
Benzaldehyde.

$$C_6H_5CCl_3 + 2H_2O = C_6H_5CO.OH + 3HCl.$$
Benzoic acid.
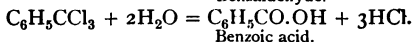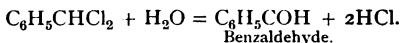
PREPARATION 78.

Benzylalcohol may be also obtained by the action of caustic potash on benzaldehyde (see Reaction 4, p 60). This reaction is specially characteristic of ring-compounds containing an aldehyde-group in the nucleus, although some of the higher aliphatic aldehydes behave in a similar fashion,

$$2C_6H_5COH + KOH = C_6H_5CH_2OH + C_6H_5COOK.$$
Benzyl alcohol.   Potassium benzoate,
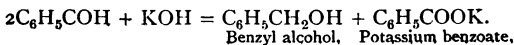
Benzyl alcohol has the properties of an aliphatic alcohol, and not those of a phenol. On oxidation, it gives benzaldehyde and benzoic acid, and it forms benzyl esters with acids or acid chlorides,

$$C_6H_5CO.OCH_2.C_6H_5.$$
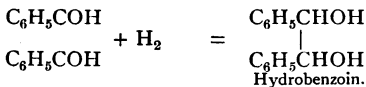Benzyl benzoate.
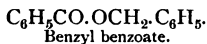
PREPARATION 79.

Benzaldehyde.—The aldehydes of the aromatic series may also be obtained by the oxidation of a methyl side-chain with chromium oxychloride. The solid brown product, $C_6H_5CH_3(CrO_2Cl_2)_2$, formed by adding CrO_2Cl_2 to toluene, dissolved in carbon bisulphide, is decomposed with water, and benzaldehyde separates out (Etard).

The numerous reactions which benzaldehyde undergoes are described in this preparation, and in some of the subsequent ones (see Preps. 80, 81, 82). In addition to these, benzaldehyde combines with hydrocyanic acid to form the cyanhydrin or mandelic nitrile,

$$C_6H_5COH + HCN = C_6H_5CH(OH).CN.$$
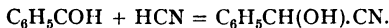
The preparation of the cyanhydrin does not always necessitate the use of hydrocyanic acid. In the formation of mandelic nitrile, a mixture of the aldehyde and powdered potassium cyanide is treated with conc. hydrochloric acid in the cold. The cyanhydrin is then separated by pouring into water, which sets free the cyanhydrin in the form of an oil (Spiegel). On hydrolysis with conc. hydrochloric acid, mandelic acid is formed.

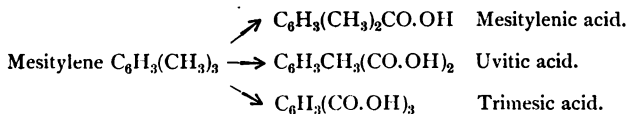On reduction, benzaldehyde yields, in addition to benzyl alcohol, a pinacone known as *hydrobenzoin*,

$$\begin{array}{l} C_6H_5COH \\ C_6H_5COH \end{array} + H_2 = \begin{array}{l} C_6H_5CHOH \\ | \\ C_6H_5CHOH \end{array}$$
Hydrobenzoin.

PREPARATION 80.

Benzoic acid.—The oxidation of the side-chains in aromatic hydrocarbons is a matter of considerable interest, as illustrating the difference of stability of the side-chain and nucleus, and also

of the influence which the relative positions of the side-chains, where more than one is present, exert in presence of oxidising agents.

The oxidation of the side-chain of an aromatic hydrocarbon, when more than one is present, takes place in successive steps. Thus mesitylene is converted into the following compounds on oxidation,

$$\text{Mesitylene } C_6H_3(CH_3)_3 \longrightarrow \begin{cases} C_6H_3(CH_3)_2CO.OH & \text{Mesitylenic acid.} \\ C_6H_3CH_3(CO.OH)_2 & \text{Uvitic acid.} \\ C_6H_3(CO.OH)_3 & \text{Trimesic acid.} \end{cases}$$

The reagents usually employed are (1) chromic acid or potassium bichromate and sulphuric acid, (2) dilute nitric acid and (3) potassium permanganate in alkaline or neutral solution. The action of these upon the side-chain, when more than one side-chain is present, depends upon their relative position. Thus, for example, potassium bichromate and sulphuric acid either does not act, or completely destroys the compound when the side-chains occupy the ortho-position (Fittig), whereas the para- and meta-compounds yield the corresponding carboxylic acids. This is true also of substituted hydrocarbons with one side-chain; thus meta- and para-nitrotoluene give meta- and para-nitrobenzoic acid. The ortho-compound with the same oxidising agent is completely destroyed. Dilute nitric acid, or potassium permanganate in alkaline solution, may be used in the oxidation of ortho- side-chains; also, on account of their less energetic action, where only one side-chain is to be converted into carboxyl.

The oxidation of a halogen-substituted side-chain is much more readily accomplished than that of a simple alkyl-group. A similar case is that of naphthalene tetrachloride, $C_{10}H_8Cl_4$, which, though an additive compound, is much more readily converted into phthalic acid than naphthalene itself.

PREPARATION 81.

Benzoin.—As a small quantity of potassium cyanide is capable of converting a large quantity of benzaldehyde into benzoin, the action of the cyanide has been explained as follows:

The potassium cyanide first reacts with the aldehyde and forms a potassium compound of the aldehyde,

$$C_6H_5COH + KCN = HCN + C_6H_5COK.$$
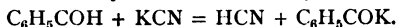
Another molecule of aldehyde unites with the hydrocyanic acid and forms mandelic nitrile,

$$C_6H_5COH + HCN = C_6H_5.CH(OH).CN.$$
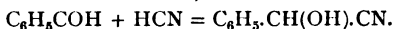
The potassium aldehyde and nitrile then combine, forming benzoin and liberating potassium cyanide, which is then able to react with a fresh portion of aldehyde (Chalanay and Knoevenagel),

$$C_6H_5CO + HO.HCC_6H_5 = C_6H_5CO.CHOH.C_6H_5 + KCN.$$
$$\quad | \quad\quad\quad\quad |$$
$$\quad K \quad\quad\quad CN$$
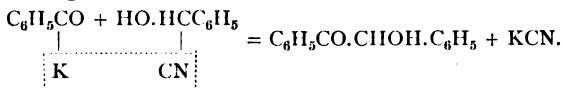
The same reaction occurs with other aromatic aldehydes (anisaldehyde, cuminol, furfurol, &c.).

Benzoin yields hydrobenzoin on reduction with sodium amalgam, and desoxybenzoin, $C_6H_5CO.CH_2.C_6H_5$, when reduced with zinc and hydrochloric acid.

The latter, which contains the group $CO.CH_2.C_6H_5$, behaves like malonic ester, the hydrogen of the methylene group being replaceable by sodium, and hence by alkyl groups.

PREPARATION 82.

Cinnamic acid.—The reaction, which takes place when an aldehyde (aliphatic or aromatic) acts on the sodium salt of an aliphatic acid in presence of the anhydride, is known as "Perkin's reaction," and has a very wide application. According to the result of Fittig's researches on the properties of the unsaturated acids described below, the reaction occurs in two steps. The aldehyde forms first an additive compound with the acid, the aldehyde carbon attaching itself to the α-carbon (*i.e.*, next the carboxyl) of the acid. A saturated oxy-acid is formed, which is stable, if the α-carbon is attached to only one atom of hydrogen, as in the case of isobutyric acid,

$$C_6H_5CHO + \frac{CH_3}{CH_3}{>}CH.COOH = C_6H_5CH(OH).\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}.COOH.$$
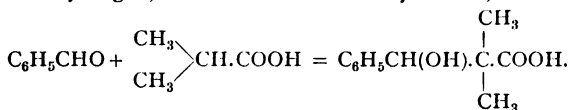
If, as in acetic and propionic acid, the group CH_2 is present in the a-position, water is simultaneously split off, and an unsaturated acid results,
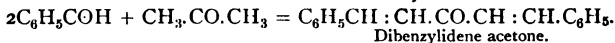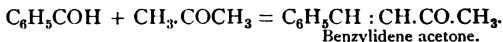
$$C_6H_5CHO + CH_3.CH_2.COOH = C_6H_5CH \underset{\substack{| \\ CH_3 \\ a\text{-Methylcinnamic acid.}}}{:} C.COOH + H_2O.$$
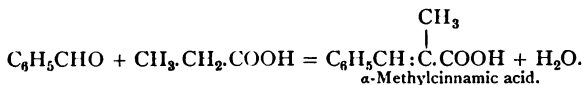
That a-methylcinnamic acid is formed and not phenylcrotonic acid according to the equation,

$$C_6H_5CHO + CH_3.CH_2.COOH = C_6H_5CH : CH.CH_2.COOH + H_2O,$$
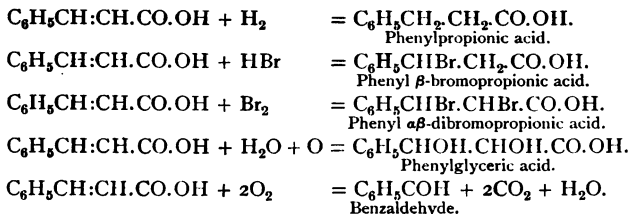$$\text{Phenylcrotonic acid.}$$
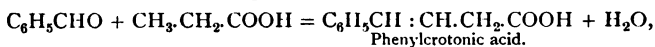
follows from Fittig's researches, and depends upon the marked difference exhibited by the two principal groups of unsaturated acids, viz., the $a\beta$ acids, which have the double link between the first and second carbon from the carboxyl, and $\beta\gamma$ acids, in which the double link lies between the second and third carbons. Methylcinnamic acid belongs to the first group, whereas phenylcrotonic acid belongs to the second group.

It may be noted in passing that this reaction bears a close resemblance to that studied by Claisen, which occurs in presence of caustic soda solution between aldehydes or ketones on the one hand, and compounds containing the group $CH_2.CO$. Benzaldehyde and acetone combine under these conditions to form benzylidene and dibenzylidene acetone,

$$C_6H_5COH + CH_3.COCH_3 = C_6H_5CH : CH.CO.CH_3.$$
$$\text{Benzylidene acetone.}$$

$$2C_6H_5COH + CH_3.CO.CH_3 = C_6H_5CH : CH.CO.CH : CH.C_6H_5.$$
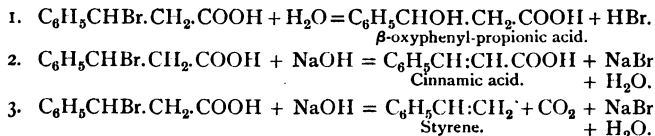$$\text{Dibenzylidene acetone.}$$

All the unsaturated acids have the following properties in common. They form additive compounds with nascent hydrogen, halogen acids, and the halogens. On oxidation with alkaline permanganate in the cold, they take up two hydroxyl groups to form a dihydroxy-derivative, and, on further oxidation, ultimately divide at the double link. Cinnamic acid may be taken by way of illustration. On reduction it forms phenylpropionic acid, with hydrobromic acid, β-bromophenylpropionic acid (the bromine attaching itself to the β-carbon, see p. 206), with bromine, $a\beta$-dibromophenylpropionic acid, on oxidation with permanganate, phenylglyceric acid and then benzaldehyde and benzoic acid.
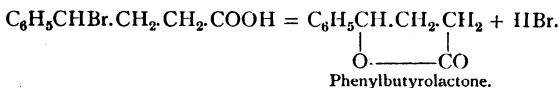
$$C_6H_5CH:CH.CO.OH + H_2 \quad = C_6H_5CH_2.CH_2.CO.OH.$$
<div align="center">Phenylpropionic acid.</div>

$$C_6H_5CH:CH.CO.OH + HBr \quad = C_6H_5CHBr.CH_2.CO.OH.$$
<div align="center">Phenyl β-bromopropionic acid.</div>

$$C_6H_5CH:CH.CO.OH + Br_2 \quad = C_6H_5CHBr.CHBr.CO.OH.$$
<div align="center">Phenyl αβ-dibromopropionic acid.</div>

$$C_6H_5CH:CH.CO.OH + H_2O + O = C_6H_5CHOH.CHOH.CO.OH.$$
<div align="center">Phenylglyceric acid.</div>

$$C_6H_5CH:CH.CO.OH + 2O_2 \quad = C_6H_5COH + 2CO_2 + H_2O.$$
<div align="center">Benzaldehyde.</div>

The chief difference between the two groups of αβ and βγ unsaturated acids lies in the behaviour of the additive compounds which they form with hydrobromic acid and bromine.

In the case of the αβ acids, the hydrobromide of the acid, on boiling with water, yields the corresponding β oxy-acid, and, on boiling with alkalis, a mixture of the original acid and the unsaturated hydrocarbon, formed by the elimination of carbon dioxide and hydrobromic acid,
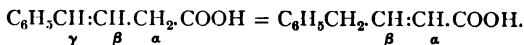
1. $C_6H_5CHBr.CH_2.COOH + H_2O = C_6H_5CHOH.CH_2.COOH + HBr.$
<div align="center">β-oxyphenyl-propionic acid.</div>

2. $C_6H_5CHBr.CH_2.COOH + NaOH = C_6H_5CH:CH.COOH + NaBr$
<div align="center">Cinnamic acid.   + H_2O.</div>

3. $C_6H_5CHBr.CH_2.COOH + NaOH = C_6H_5CH:CH_2 + CO_2 + NaBr$
<div align="center">Styrene.   + H_2O.</div>

The hydrobromides of βγ unsaturated acids like β-phenyl-crotonic acid behave quite differently. On boiling with water, lactones are formed, i.e., inner anhydrides of oxy-acids,

$$C_6H_5CHBr.CH_2.CH_2.COOH = C_6H_5CH.CH_2.CH_2 + HBr.$$
$$| \quad\quad\quad\quad |$$
$$O.\text{———}CO$$
<div align="center">Phenylbutyrolactone.</div>

The readiest method for distinguishing a βγ-acid, especially of the aliphatic series, is to heat the acid with a mixture of equal volumes of conc. sulphuric acid and water to about 140°. The lactone is formed if a βγ-acid is present, whereas an αβ-acid remains unchanged. By diluting, neutralising with sodium carbonate, and extracting with ether, the lactone is separated, the αβ-acid remaining in solution.

An interesting relation exists between the two groups of acids. It has been found that, on heating βγ-acids with caustic

soda solution, a shifting of the double link to the $\alpha\beta$-position takes place,

$$C_6H_5CH{:}CH.CH_2.COOH = C_6H_5CH_2.CH{:}CH.COOH.$$
$$\quad\;\;\gamma\quad\;\beta\quad\alpha\qquad\qquad\qquad\qquad\beta\quad\;\alpha$$

PREPARATION 85.

Benzoyl chloride.—The formation of esters by the action of benzoyl chloride or other acid chloride on an alcohol or phenol in presence of caustic soda is known as the "Schotten-Baumann reaction." The reaction may also be employed in the preparation of derivatives of the aromatic amines containing an acid radical, like benzanilide, $C_6H_5NH.CO.C_6H_5$,

$$C_6H_5COCl + NH_2.C_6H_5 + NaOH = C_6H_5CO.NHC_6H_5 + NaCl + H_2O.$$
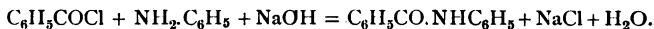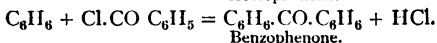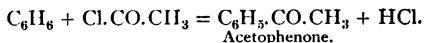
PREPARATION 86.

Ethyl benzoate.—The method of Fischer and Speier for the preparation of esters, by boiling together the acid with the alcohol containing about 3 per cent. of either hydrochloric acid or conc. sulphuric acid, can be adopted in the majority of cases with good results, and has many advantages over the old method of passing hydrochloric acid gas into a mixture of the alcohol and acid until saturated. Read Notes on Prep. 15, p. 201.

PREPARATION 87.

Acetophenone.—"Friedel and Crafts' reaction," of which this preparation is a type, consists in the use of anhydrous aluminium chloride for effecting combination between an aromatic hydrocarbon or its derivative on the one hand, and a halogen (Cl or Br) compound on the other. The reaction is always accompanied by the evolution of hydrochloric or hydrobromic acid, and the product is a compound with $AlCl_3$, which decomposes and yields the new substance on the addition of water. This reaction has been utilised, as in the present case, (1) for the preparation of ketones, in which an acid chloride (aliphatic or aromatic) is employed,

$$C_6H_6 + Cl.CO.CH_3 = C_6H_5.CO.CH_3 + HCl.$$
$$\text{Acetophenone.}$$
$$C_6H_6 + Cl.CO\ C_6H_5 = C_6H_6.CO.C_6H_6 + HCl.$$
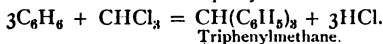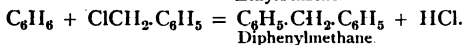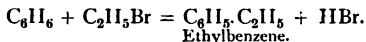$$\text{Benzophenone.}$$

If a substituted aromatic hydrocarbon is used, the ketone group then enters the para-position, or, if this is occupied, the ortho-position. Substituted aromatic acid chlorides may also be used, and if the acid is dibasic and has two carboxyl chloride groups, two molecules of the aromatic hydrocarbon may be attached. If phosgene is used with two molecules of benzene, benzophenone is obtained,
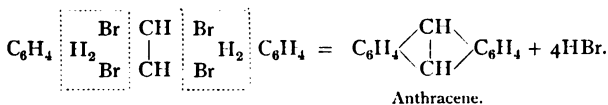
$$2C_6H_6 + Cl_2CO = C_6H_5.CO.C_6H_5 + 2HCl.$$
<div align="center">Benzophenone.</div>

(2) This reaction may be modified by decreasing the proportion of the hydrocarbon, and an acid chloride is then formed,

$$C_6H_6 + ClCOCl = C_6H_5.COCl + HCl.$$
<div align="center">Benzoyl chloride.</div>
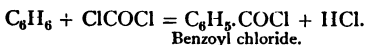
(3) With an aromatic hydrocarbon and a halogen derivative of an aliphatic hydrocarbon or aromatic hydrocarbon substituted in the side-chain, new hydrocarbons may be built up (see Prep. 89, p. 178),

$$C_6H_6 + C_2H_5Br = C_6H_5.C_2H_5 + HBr.$$
<div align="center">Ethylbenzene.</div>

$$C_6H_6 + ClCH_2.C_6H_5 = C_6H_5.CH_2.C_6H_5 + HCl.$$
<div align="center">Diphenylmethane.</div>

$$3C_6H_6 + CHCl_3 = CH(C_6H_5)_3 + 3HCl.$$
<div align="center">Triphenylmethane.</div>

Anthracene has been synthesised from tetrabromethane and benzene by this method,

$$C_6H_4 \begin{matrix} Br \\ H_2 \\ Br \end{matrix} \begin{matrix} CH \\ | \\ CH \end{matrix} \begin{matrix} Br \\ H_2 \\ Br \end{matrix} C_6H_4 = C_6H_4 \underset{CH}{\overset{CH}{\Big\langle}} {\Big|} {\Big\rangle} C_6H_4 + 4HBr.$$
<div align="center">Anthracene.</div>

(4) Acid amides may be prepared by the use of chloroformamide,

$$C_6H_6 + ClCONH_2 = C_6H_5.CO.NH_2 + HCl.$$
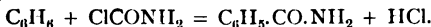
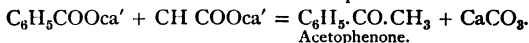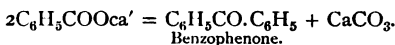The chloroformamide is obtained by passing HCl gas over heated cyanuric acid (Gattermann),

$$HOCN + HCl = Cl.CONH_2.$$
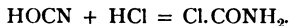
(5) Oxyaldehydes have been obtained indirectly by the use of the crystalline compound HCl.HCN, which hydrochloric acid forms with hydrocyanic acid, acting upon a phenol ether,

$$C_6H_5OCH_3 + HCl.HCN = C_6H_4 \begin{cases} OCH_3 \\ CH : NH. \end{cases}$$

The aldime is subsequently hydrolysed with dilute sulphuric acid (Gattermann),

$$C_6H_4 \begin{cases} OCH_3 \\ C : NH \end{cases} + H_2O = C_6H_4 \begin{cases} OCH_3 \\ COH \end{cases} + NH_3.$$
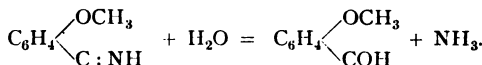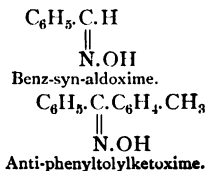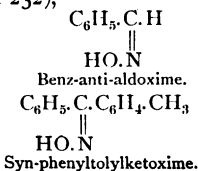
In addition to Friedel and Crafts' reaction, the aromatic ketones may be obtained by distilling the calcium salt of the aromatic acid or a mixture of the salts of an aromatic and aliphatic acid. The reaction is precisely analogous to the process used for the preparation of aliphatic ketones,

$$2C_6H_5COOca' = C_6H_5CO.C_6H_5 + CaCO_3.$$
Benzophenone.

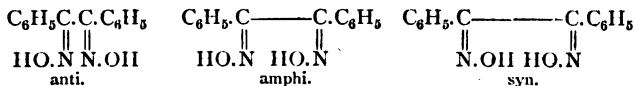$$C_6H_5COOca' + CH\ COOca' = C_6H_5.CO.CH_3 + CaCO_3.$$
Acetophenone.

They possess the usual properties of ketones of the aliphatic series (see p. 194), which are illustrated by the various reactions described at the end of this preparation.
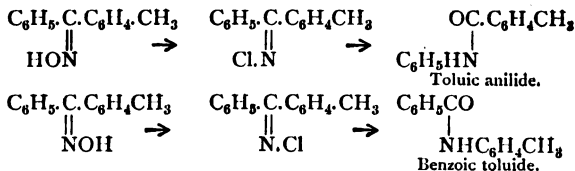
A special interest attaches to the oximes of the aldehydes and of those ketones which contain two different radicals linked to the CO group. Many of these substances exist in two isomeric forms, which are readily converted into one another. Benzaldoxime and phenyltolylketoxime exist in two forms and benzildioxime in three forms, which cannot be explained on structural differences of constitution. They must therefore represent different space configurations of a type analogous to that of citraconic and mesaconic acid (Hantzsch). They are distinguished by the terms "syn" and "anti," corresponding to "cis" and "trans" among the unsaturated acids. "Anti" signifies away from the group, the name of which follows ; "syn" signifies the position near that group (see pp. 217 and 232),

$$C_6H_5.C.H$$
$$\|$$
$$HO.N$$
Benz-anti-aldoxime.

$$C_6H_5.C.H$$
$$\|$$
$$N.OH$$
Benz-syn-aldoxime.

$$C_6H_5.C.C_6H_4.CH_3$$
$$\|$$
$$HO.N$$
Syn-phenyltolylketoxime.

$$C_6H_5.C.C_6H_4.CH_3$$
$$\|$$
$$N.OH$$
Anti-phenyltolylketoxime.

Benzil forms three dioximes which are distinguished by the names "syn," "anti," and "amphi."

$$C_6H_5C.C.C_6H_5 \qquad C_6H_5.C\text{———}C.C_6H_5 \qquad C_6H_5.C\text{———}C.C_6H_5$$
$$\underset{\text{anti.}}{\underset{\text{HO.N}}{\|} \underset{\text{N.OH}}{\|}} \qquad \underset{\text{amphi.}}{\underset{\text{HO.N}}{\|} \underset{\text{HO.N}}{\|}} \qquad \underset{\text{syn.}}{\underset{\text{N.OH}}{\|} \underset{\text{HO.N}}{\|}}$$

The action of PCl_5 on these substances, known as Beckmann's reaction, is of great importance in distinguishing the different forms of ketoximes. The two isomeric phenyltolyl-ketoximes yield two different amides,

$$\underset{\text{HON}}{C_6H_5.C.C_6H_4.CH_3} \rightarrow \underset{\text{Cl.N}}{C_6H_5.C.C_6H_4CH_3} \rightarrow \underset{\underset{\text{Toluic anilide.}}{C_6H_5HN}}{OC.C_6H_4CH_3}$$

$$\underset{\text{NOH}}{C_6H_5.C.C_6H_4CH_3} \rightarrow \underset{\text{N.Cl}}{C_6H_5.C.C_6H_4.CH_3} \rightarrow \underset{\underset{\text{Benzoic toluide.}}{NHC_6H_4CH_3}}{C_6H_5CO}$$

Toluic anilide, on hydrolysis, forms toluic acid and aniline, whereas benzoic toluide yields benzoic acid and toluidine. It follows therefore that, in the original compound, the first contains the hydroxyl nearer the phenyl group and the second nearer the tolyl group.

For further details on the stereoisomerism of nitrogen compounds, the text-book must be consulted.

PREPARATION 88.

Diphenylmethane.—This reaction is analogous to that of aluminium chloride on a mixture of benzene and benzyl chloride referred to in the Notes on Prep. 87, p. 254. The reaction is also effected by the use of zinc dust or finely-divided copper (Zincke).
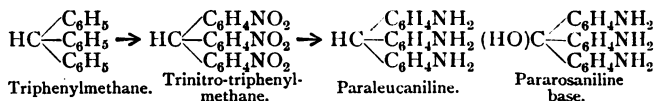
PREPARATION 89.

Triphenylmethane.—This is another example of "Friedel and Crafts'" reaction, which has already been referred to in the Notes on Prep. 87, p. 254.

The synthesis of pararosaniline from triphenylmethane is one which has gone far to solve the problem of the constitution of the important class of triphenylmethane colouring matters.

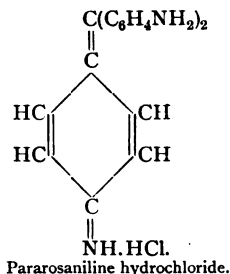Rosaniline or magenta was originally obtained by oxidising

COHEN'S ADV. P. O. C. S

with arsenic acid a mixture of aniline with ortho- and para-toluidine. The product was then lixiviated and treated with common salt, which converted the arsenate into the hydrochloride of rosaniline. Pararosaniline was prepared in a similar way from a mixture of aniline and para-toluidine. The series of reactions by which triphenylmethane is converted into pararosaniline may be represented as follows :—
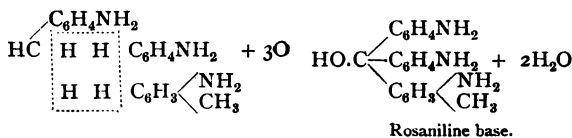
$$HC\!\!\begin{array}{l}\diagup C_6H_5 \\ \!\!-C_6H_5 \\ \diagdown C_6H_5\end{array} \rightarrow HC\!\!\begin{array}{l}\diagup C_6H_4NO_2 \\ \!\!-C_6H_4NO_2 \\ \diagdown C_6H_3NO_2\end{array} \rightarrow HC\!\!\begin{array}{l}\diagup C_6H_4NH_2 \\ \!\!-C_6H_4NH_2 \\ \diagdown C_6H_4NH_2\end{array} (HO)C\!\!\begin{array}{l}\diagup C_6H_4NH_2 \\ \!\!-C_6H_4NH_2 \\ \diagdown C_6H_4NH_2\end{array}$$

Triphenylmethane.   Trinitro-triphenyl-methane.   Paraleucaniline.   Pararosaniline base.

By the action of hydrochloric acid on the base, the hydrochloride of pararosaniline is formed, which is the soluble colouring matter.

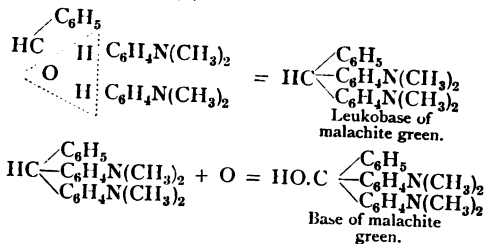$$HO.C(C_6H_4NH_2)_3 + HCl = C(C_6H_4NH_2)_3Cl + H_2O.$$
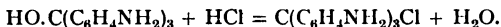
The constitution of the hydrochloride is doubtful ; but the so-called *quinonoid* structure, by which the substance is represented as a derivative of quinone, is generally accepted.

$$
\begin{array}{c}
C(C_6H_4NH_2)_2 \\
\parallel \\
C \\
\end{array}
$$

HC ⟨hexagon⟩ CH
HC ⟨hexagon⟩ CH

$$
\begin{array}{c}
C \\
\parallel \\
NH.HCl.
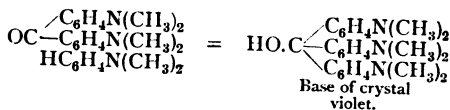\end{array}
$$

Pararosaniline hydrochloride.

The formation of rosaniline from the mixture of aniline, ortho- and para-toluidine is represented by assuming that the methyl-group of para-toluidine acts as the link which connects the nuclei of aniline and ortho-toluidine.

$$HC\begin{array}{|c|} \diagup C_6H_4NH_2 \\ \hline H\ H\ \ C_6H_4NH_2 \\ H\ H\ \ C_6H_3\!\!\diagup^{NH_2}_{CH_3} \\ \hline \end{array} + 3O \qquad HO.C\begin{array}{l} C_6H_4NH_2 \\ -C_6H_4NH_2 \\ C_6H_3\!\!\diagup^{NH_2}_{CH_3} \end{array} + 2H_2O$$

Rosaniline base.

The formation of malachite green (benzaldehyde green) by the action of benzaldehyde upon dimethylaniline in presence of zinc chloride, and subsequent oxidation of the product, may be interpreted on similar lines, and has already been referred to. (See Notes on Prep. 53, p. 229.)

$$HC \overset{C_6H_5}{\underset{O}{\diagup}} \begin{matrix} H : C_6H_4N(CH_3)_2 \\ H : C_6H_4N(CH_3)_2 \end{matrix} = HC \overset{C_6H_5}{\underset{C_6H_4N(CH_3)_2}{\diagdown}} C_6H_4N(CH_3)_2$$

Leukobase of
malachite green.

$$HC \overset{C_6H_5}{\underset{C_6H_4N(CH_3)_2}{\diagdown}} C_6H_4N(CH_3)_2 + O = HO.C \overset{C_6H_5}{\underset{C_6H_4N(CH_3)_2}{\diagdown}} C_6H_4N(CH_3)_2$$

Base of malachite
green.

The preparation of "crystal violet" from Michler's compound and dimethylaniline in presence of $POCl_3$ may be explained in a similar fashion.

$$OC \overset{C_6H_4N(CH_3)_2}{\underset{HC_6H_4N(CH_3)_2}{\diagdown}} C_6H_4N(CH_3)_2 = HO.C \overset{C_6H_4N(CH_3)_2}{\underset{C_6H_4N(CH_3)_2}{\diagdown}} C_6H_4N(CH_3)_2$$

Base of crystal
violet.

The constitution of the hydrochlorides of malachite green and crystal violet will appear as follows :—

Malachite green.

Crystal violet.
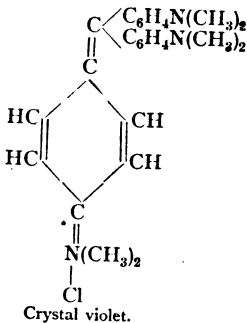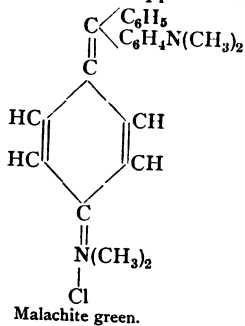
PREPARATION 90 AND 91.

Naphthalene Sulphonate of Sodium, β-Naphthol.—

The formation of the sulphonic acid of naphthalene and the

corresponding phenol by fusion with caustic soda is analogous to that of benzene sulphonic acid and phenol (see Prep. 67, p. 152, and 69, p. 154). It should be noted that naphthalene forms two series of mono-derivatives distinguished as α and β compounds. By the action of sulphuric acid on naphthalene, both α and β sulphonic acids are formed. At a lower temperature (100°) the product consists mainly of the α compound ; at a higher temperature (170°) of the β compound. β-Naphthol and its derivatives are used for the preparation of azo-colours (see Reaction 5, p. 141), and for that of β-naphthylamine. The latter is obtained by the action of ammonia under pressure on β-naphthol,

$$C_{10}H_7OH + NH_3 = C_{10}H_7NH_2 + H_2O.$$
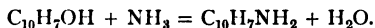
This reaction is resorted to for the reason that naphthalene forms only the α-nitro-compound with nitric acid. The method, similar to that used for preparing aniline from nitrobenzene, cannot, therefore, be employed for the production of β-naphthylamine. α-Naphthol is mainly used for the manufacture of yellow and orange colours (Martius and naphthol orange) by the action of nitric acid, and are similar in constitution to picric acid.

The naphthols differ from the phenols of the benzene series in forming ethers after the manner of aliphatic alcohols, viz., by the action of sulphuric acid on a mixture of the naphthol and the alcohol, which the other phenols do not.

$$C_{10}H_7OH + CH_3OH = C_{10}H_7OCH_3 + H_2O$$
$$\text{Naphthyl methyl ether.}$$
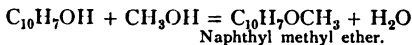
PREPARATION 92.

Anthraquinone.—The constitution of anthraquinone is derived from various syntheses, such as the action of zinc dust on a mixture of phthalyl chloride and benzene, or by heating benzoyl benzoic acid with P_2O_5.

$$C_6H_4 \begin{matrix} COCl \\ COCl \end{matrix} + C_6H_6 = C_6H_4 \begin{matrix} CO \\ CO \end{matrix} C_6H_4 + 2HCl.$$

$$C_6H_4 \begin{matrix} CO.C_6H_5 \\ COOH \end{matrix} = C_6H_4 \begin{matrix} CO \\ CO \end{matrix} C_6H_4 + H_2O.$$
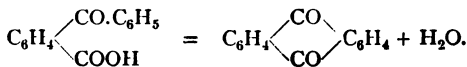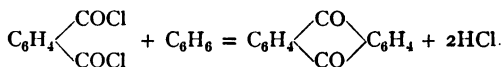
Unlike benzoquinone, it is not reduced by sulphur dioxide (see Prep. 76, p. 163). Heated with HI or zinc dust it is converted into anthracene.

PREPARATION 94.

Alizarin.—The first synthesis of alizarin is due to Graebe and Liebermann (1868). The present method was discovered simultaneously by these chemists and by Perkin. By the action of fuming sulphuric acid on anthraquinone, the main product is β-anthraquinone monosulphonic acid,
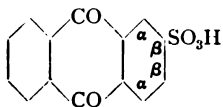

By fusion of the sodium salt with caustic soda and potassium chlorate, the hydroxyl groups enter the a and β position. The constitution of alizarin is therefore
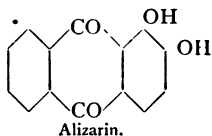
Alizarin.

The constitution has been determined by its synthesis from phthalic anhydride and catechol in presence of concentrated sulphuric acid (Baeyer).

$$C_6H_4{<}^{CO}_{CO}{>}O + C_6H_4{<}^{OH\ \ 1}_{OH\ \ 2} = C_6H_4{<}^{CO}_{CO}{>}C_6H_2{<}^{OH\ \ 1}_{OH\ \ 2}$$
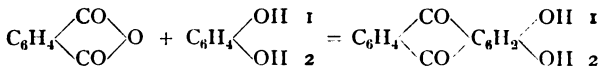
Other colouring matters have been obtained by the oxidation of alizarin (purpurin), and by fusion of the disulphonic acids of anthraquinone with caustic soda (anthrapurpurin and flavopurpurin). It is an interesting fact that, among the numerous di- and poly-hydroxyanthraquinones, only those which have the two hydroxyls in the $a\beta$ position are colouring matters (Liebermann and Kostanecki).
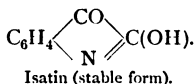
Purpurin.

Anthrapurpurin.

Flavopurpurin.
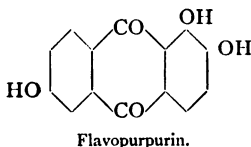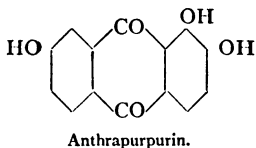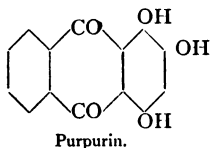
PREPARATION 95.

Isatin.—The formation of isatin from indigo may be represented as follows :—
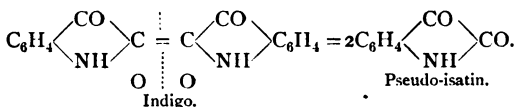
This compound represents the unstable pseudo- or lactam-form, and passes into the stable or lactim-form (Baeyer).

$$C_6H_4 \diagleft{\substack{CO \\ N}} C(OH).$$

Isatin (stable form).

There exists, however, some uncertainty as to which formula represents the stable form. Derivatives of both forms are known, and the compound offers an example of *tautomerism* (see Notes on Preps. 16, p. 202, and 49, p. 228), or, as it has been also termed, *pseudomerism*.
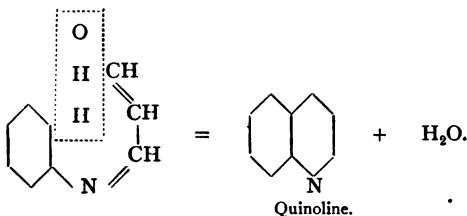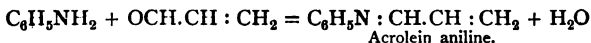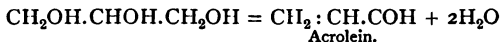
The constitution of isatin has been determined by its synthesis from ortho nitrophenylglyoxylic acid,
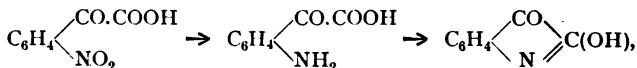
which passes on reduction into the amido-compound, the latter forming the anhydride or isatin (Claisen).

PREPARATION 96.

Quinoline.—The formation of quinoline by " Skraup's reaction" may be explained as follows: The sulphuric acid converts the glycerin into acrolein, which then combines with the aniline to form acrolein aniline. The latter on oxidation with nitrobenzene yields quinoline.

$$CH_2OH.CHOH.CH_2OH = CH_2 : CH.COH + 2H_2O$$
Acrolein.

$$C_6H_5NH_2 + OCH.CH : CH_2 = C_6H_5N : CH.CH : CH_2 + H_2O$$
Acrolein aniline.

Quinoline.

The reaction is a very general one, and most of the primary aromatic amines and their derivatives can be converted into quinoline derivatives, provided that one ortho-position to the amido-group is free. Ortho-amidophenol, for example, yields ortho-oxyquinoline in the same way.

Ortho-amidophenol.   Ortho-oxyquinoline.
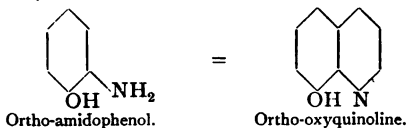
PREPARATION 97.

Quinine.—There is no general method by which the alkaloids can be isolated from the plants in which they are found. They usually exist in combination with acids, such as malic, lactic, and other common vegetable acids. Frequently the acid present is peculiar to the plant in which it occurs. Quinine and the other cinchona alkaloids are found in

combination with quinic acid, morphine with meconic acid, aconitine with aconitic acid, &c. A common method for separating the alkaloid is to add an alkali. If the base is volatile in steam, like coniine, it is distilled with water ; if, as generally happens, the substance is non-volatile, it is extracted by means of a suitable volatile solvent, such as ether, chloroform, alcohol, amyl alcohol, &c. The solvent is then distilled off and the alkaloid, which remains, is either crystallised or converted into a crystalline salt.

The constitution of quinine is not yet elucidated. Its relationship to quinoline has long been known, since it gives this substance on distillation with caustic potash (Gerhardt).

HINTS ON THE INVESTIGATION OF ORGANIC SUBSTANCES

The Elements.—Heat a portion on platinum foil and determine the nature of the residue (inorganic), if any, when the carbon has burnt away. A metallic oxide or carbonate may indicate the presence of an organic acid.

Heat a little of the substance in a small, dry test-tube and observe whether the substance melts, chars, explodes, sublimes or volatilises ; also notice the smell.

Test for nitrogen, sulphur, halogen, &c.

The presence of nitrogen may indicate an *ammonium salt, organic base (amine or alkaloid), amide, cyanide, isocyanide, nitroso- or nitro-compound, azo-compound,* &c.

The presence of sulphur may indicate a *sulphate of an organic base, alkyl sulphate, sulphite, sulphonic acid, bisulphite compound of aldehyde* or *ketone,* &c.

The presence of a halogen may indicate *haloid salt of a base, alkyl* or *alkylene halide, acid halide, haloid derivative of an acid,* &c.

Homogeneity.—Determine if the substance is homogeneous. If it is a liquid, distil a few c. c. from a miniature distilling flask with long side tube, but no condenser. Use a thermometer and collect the distillate in a test-tube. Note the boiling-point, and observe if it fluctuates or remains constant and if any solid residue remains. A low boiling-point generally indicates a low molecular weight.

If the substance is a solid, examine a few particles on a slide under the microscope, or, better still, recrystallise a little and notice if the crystals appear similar in shape. If it is a mixture, try to separate the constituents by making a few trials with different solvents, water, alcohol, ether, benzene, petroleum spirit, &c. If the substance is homogeneous, determine the melting-point.

Solubility.—Try if the substance dissolves in cold or hot water. Apart from the salts of organic bases and acids, many of which are very soluble in water, the solubility of simple organic

substances is generally determined by the presence of the OH group (including CO.OH and SO_2.OH groups). The greater the proportion of OH groups to carbon, the greater, as a rule, is the solubility in water. The lower alcohols, methyl, ethyl, and propyl alcohols are miscible with water ; normal butyl and isobutyl alcohol (fermentation) dissolve in about 10 parts of water ; amyl alcohol (fermentation) in about 40 parts of water. The first two (methyl and ethyl) may be separated from solution by the addition of potassium carbonate. The addition of common salt is sufficient to separate the last three (propyl, butyl and amyl). The polyhydric alcohols, glycol, glycerin and also substances like the sugars, are extremely soluble, for the proportion of OH groups to carbon is high. Phenol requires for solution 15 parts of water, whereas the di- and tri-hydric phenols readily dissolve. The same applies to acids. The lower monobasic aliphatic acids (formic, acetic, propionic and normal butyric) are easily soluble in water, whereas isobutyric requires 3 parts and valeric about 30 parts of water. The last three separate from water on the addition of salt.

None of the aromatic acids are very soluble in water, the hydroxy and dibasic acids are more soluble than the monobasic acids at the ordinary temperature. 1,000 parts of water dissolve about $2\frac{1}{2}$ parts of benzoic, $2\frac{1}{4}$ parts of salicylic, 8 parts of phthalic and 159 parts of mandelic acid. The sulphonic acids and also many of their salts are very soluble. The lower aliphatic amines and amides are soluble in water, but not the higher members nor the simple aromatic amines. If the substance is soluble in water, it may be one of the above-named compounds, or a lower aldehyde or ketone, or a salt of a base or acid.

The following groups of compounds are generally insoluble in water : hydrocarbons (lighter than water), halogen and nitro-compounds (heavier than water), ethers and esters of organic acids (lighter or heavier than water). The above preliminary investigation will determine the further course of investigation, but the following rough plan may serve as a guide.

§ I. Single Substance, Soluble in Water.—

1. *Contains only carbon, hydrogen, and oxygen.*—The number of such substances is comparatively small. It may be an *alcohol, sugar, acid,* or *phenol* or *aldehyde* and *ketone* of low molecular weight. Make a solution and test with litmus. If the liquid

is acid, a free *acid* is probably present. If the liquid is neutral and a metal has been found, a metallic salt is probably present. The separation and identification of the acid is not a very simple matter. If the acid is an aromatic or an aliphatic acid of high molecular weight, a few drops of conc. hydrochloric acid will usually precipitate it and it may then be filtered or removed with ether and its melting-point determined. If it is volatile (formic acetic, butyric, &c.) the solution should be acidified with sulphuric acid and distilled. The distillate will contain the free acid. Individual tests may then be directly applied, but it is preferable to neutralise the distillate with caustic soda and evaporate to dryness on the water-bath, so as to obtain the sodium salt before testing. The acid may be soluble and non-volatile like oxalic, tartaric, succinic, citric, &c., and then special tests must be applied (see tests for these acids). If it is a free *phenol*, ether will extract it from its aqueous solution. When the ether has been removed, tests with ferric chloride, &c., will identify ordinary phenol, resorcinol, &c. It may be a liquid *alcohol* (methyl, ethyl, propyl, &c.). Its boiling-point will have already been determined. It may be further identified by converting it into the benzoic ester and determining the b.p. of the ester (see Reaction 2, p. 174). Glycerin will be identified by its viscid character and reactions (see p. 93). If the alcohol is in aqueous solution, it will separate on the addition of potassium carbonate. Glycerin in aqueous solution may be separated by evaporation on the water-bath.

A *sugar* will char on heating. It is tested with alkaline copper sulphate, ammonio-silver nitrate or phenylhydrazine acetate. Cane sugar will not give these reactions until it has been boiled for a minute with a few drops of dilute sulphuric acid and inverted (see Prep. 41 and Notes).

Aldehydes and *ketones* are detected in the first instance by (1) shaking with a cold saturated solution of sodium bisulphite (see Reaction 2, p. 60), (2) adding to the aqueous solution a solution of phenylhydrazine acetate (see Reaction, p. 110). The aldehyde may be distinguished from the ketone by its reducing action on ammonio-silver nitrate solution and by Schiff's test (see Reactions, p. 60).

2. *Contains nitrogen.*—Add caustic soda solution and warm. If an *ammonium salt* is present, ammonia will be given off; if

the salt of an insoluble organic base is present (*amine, alkaloid*) it may be precipitated as a liquid or solid.

A soluble organic base (*lower amine*) will be detected by its smell. The identification of primary, secondary and tertiary amines is described under § II., 2.

Acid amides and cyanides are decomposed by hot concentrated caustic soda solution, by concentrated hydrochloric acid or sulphuric acid (50 per cent.). In the first case, ammonia is evolved, in the latter two cases, salts of ammonia are formed, which yield ammonia on heating with excess of caustic soda.

3. *Contains halogen.*—It may be a halogen acid (*e.g.* chloracetic acid) or the hydrochloride of a base. In the former case, it will have an acid reaction, and the solution will remain clear on adding caustic soda. In the latter case, on adding caustic soda, the base will be precipitated as solid or liquid, or, if volatile, possess a strong ammoniacal smell.

4. *Contains sulphur.*—Heat with dilute hydrochloric acid. The bisulphite compound of an aldehyde or ketone will be decomposed and sulphur dioxide evolved. An alkyl acid sulphate will also be decomposed and free sulphuric acid will be found in solution (see Reaction 2, p. 47). If the aldehyde or ketone is volatile, distil with dilute sulphuric acid and test the distillate. If the substance is an ester of sulphuric or sulphurous acid, distil with moderately concentrated caustic soda solution and test the distillate for an alcohol. If an aromatic sulphonic acid is present, a phenol will be obtained on fusion with potash (see Preps. 69 and 90).

§ II. **Single Substance, Insoluble in Water.**—This category includes the majority of organic compounds.

1. *Contains only carbon and hydrogen, or carbon, hydrogen, and oxygen.*

Liquids.—It may be a *hydrocarbon* (paraffin, olefine, aromatic), *ester*, *higher alcohol* (*e.g.* amyl alcohol), *aldehyde* (*e.g.* benzaldehyde), or *acid* (*e.g.* valeric acid). The action of sodium when testing for the elements will already have indicated the hydrocarbon by its inertness. It may be an *ester*. Boil a few c.c. of the liquid with 3—4 volumes of strong caustic potash ($1KOH:3H_2O$), using an upright condenser (see Reaction, p. 74), and notice if the liquid diminishes in bulk.

An ester will be completely hydrolysed. If the alcohol is soluble in water, a clear solution will be obtained. Distil the liquid, using a thermometer. The alcohol, if volatile, will pass into the receiver, whilst the acid remains as the potassium salt in the distilling vessel. The alcohol is separated by adding potassium carbonate, and its boiling-point and that of its benzoic ester determined; the acid is treated as described under § I., 1. If the substance is a fat or oil (*i.e.*, non-volatile, which decomposes on heating, turning brown, and evolving the smell of acrolein), then the hydrolysis is carried out with methyl-alcoholic potash ($1KOH:19CH_3OH$) in place of aqueous potash. After hydrolysis, the alcohol is evaporated on the water-bath, the residue dissolved in water, and the acid set free by hydrochloric acid. The acid is filtered, if solid; extracted with ether, if liquid; or distilled if soluble and volatile (butyric acid), and the remaining liquid evaporated to dryness. The glycerin is then extracted with alcohol and the alcoholic solution evaporated on the water-bath. The viscid residue is glycerin. The tests for glycerin may then be applied. If the substance resists the action of caustic potash, it may be a *hydrocarbon*. The immediate decolorisation of bromine water will identify it as an unsaturated hydrocarbon. A paraffin may be distinguished from an aromatic hydrocarbon by treating the liquid with a mixture of concentrated sulphuric and nitric acids (see p. 126). The product is then poured into water. If the product sinks as a yellow liquid or solid, it is probably a nitro-compound, and the original hydrocarbon is aromatic. If it floats unchanged on the surface of the water, it is probably a paraffin. An aromatic hydrocarbon also dissolves in fuming sulphuric acid, and does not separate out on pouring the solution into water. A paraffin is unacted on.

Solids.— The process of investigation is similar to that described under *liquids*. A free acid may be at once identified by its solubility in a solution of caustic alkali, and by being reprecipitated with concentrated hydrochloric acid. If a metal has been discovered in the preliminary examination, a careful examination must be made for an organic acid. Boil the compound with sodium carbonate solution. The sodium salt of the acid passes into solution and the metallic carbonate is precipitated. Filter; boil the filtrate with a slight excess of

nitric acid, add excess of ammonia and boil until neutral. Tests may then be applied in order to identify one of the common organic acids ; but beyond this it is impossible to carry the investigation in a limited time.

2. *Contains nitrogen.*—If it is a base or amine, it will probably dissolve in dilute hydrochloric acid and yield a chloroplatinate with platinic chloride. Some aromatic bases like diphenylamine are not very soluble in acids. Many of the common alkaloids, when dissolved in hydrochloric acid (avoid excess), give a brown amorphous precipitate with iodine solution.

Primary, secondary and *tertiary amines* may be distinguished as follows : To a solution of the base in dilute hydrochloric acid add a few drops of sodium nitrite solution. In the case of primary aliphatic amines, a rapid evolution of nitrogen will at once occur ; a primary aromatic amine at first gives a clear solution of the diazo-salt, which evolves nitrogen and turns darker on warming. The effervescence, due to the liberation of nitrous fumes, is easily distinguished from that of nitrogen, which goes on uninterruptedly, even when the liquid is removed from the flame.

After the solution of the diazo-salt has been decomposed by warming, the phenol which has been produced may be extracted with ether, the ether evaporated, and the phenol identified by special tests. A solution of the diazo-salt, when poured into a solution of β-naphthol in caustic soda, will usually give a red azo-colour. The original amine, if liquid, may sometimes be identified by warming with a little acetyl chloride and converting it into the solid acetyl derivative, which is recrystallised and the melting-point determined (see Reaction 3, p. 68).

In the case of a secondary base, the above treatment with hydrochloric acid and sodium nitrite will give an insoluble nitrosamine (liquid or solid), which is frequently yellow. It may be separated by ether and, after removing the ether, tested by Liebermann's nitroso-reaction (see Reaction 3, p. 137). Nitrous acid has no action on tertiary aliphatic amines, but forms nitroso-bases with tertiary aromatic amines (see p. 136), which dissolve in water in presence of hydrochloric acid, with which they form soluble hydrochlorides. Tertiary amines also combine with methyl iodide on warming (see Reaction, p. 135), but not with acetyl chloride.

I.—TABLE OF THE ATOMIC WEIGHTS OF THE ELEMENTS.

Element.	Symbol.	Atomic Weight.	Element.	Symbol.	Atomic Weight.
Aluminium . . .	Al.	27·1	Nickel	Ni.	58·7
Antimony . . .	Sb.	120	Niobium	Nb.	94
Arsenic	As.	75	Nitrogen	N.	14·04
Barium	Ba.	137·4	Osmium	Os.	191
Beryllium . . .	Be.	9·1	Oxygen	O.	16
Bismuth	Bi.	206·9	Palladium . . .	Pd.	106
Boron	B.	11	Phosphorus . . .	P.	31
Bromine	Br.	79·96	Platinum	Pt.	194·8
Cadmium . . .	Cd.	112	Potassium . . .	K.	39·15
Caesium	Cs.	133	Rhodium	Rh.	103
Calcium	Ca.	40	Rubidium . . .	Rb.	85·4
Carbon	C.	12	Ruthenium . . .	Ru.	101·7
Cerium	Ce.	140	Scandium . . .	Sc.	44·1
Chlorine . . .	Cl.	35·45	Selenium	Se.	79·1
Chromium . . .	Cr.	52·1	Silicon	Si.	28·4
Cobalt	Co.	59	Silver	Ag.	107·93
Copper	Cu.	63·6	Sodium	Na.	23·05
Fluorine	F.	19	Strontium . . .	Sr.	87·6
Gallium	G.	70	Sulphur	S.	32·06
Germanium . . .	Ge.	72	Tantalum . . .	Ta.	183
Gold	Au.	197·2	Tellurium . . .	Te.	127
Hydrogen	H.	1·01	Thallium	Tl.	204·1
Indium	In.	114	Thorium	Th.	232
Iodine	I.	126·85	Tin	Sn.	118·5
Iridium	Ir.	193	Titanium	Ti.	48·1
Iron	Fe.	56	Tungsten	W.	184
Lanthanum . . .	La.	138	Uranium	U.	239·5
Lead	Pb.	206·9	Vanadium	V.	51·2
Lithium	Li.	7·03	Ytterbium . . .	Yb.	173
Magnesium . . .	Mg.	24·36	Yttrium	Y.	89
Manganese . . .	Mn.	55	Zinc	Zn.	65·4
Mercury	Hg.	200·3	Zirconium	Zr.	90·6
Molybdenum . .	Mo.	96			

VAPOUR TENSION OF WATER FROM 5° TO 20°.

t	Tension.	t	Tension.	t	Tension.	t	Tension.
5.0	6.507	9.0	8.548	13.0	11.137	17.0	14.395
.1	.552	.1	.606	.1	.210	.1	.486
.2	.597	.2	.664	.2	.283	.2	.578
.3	.643	.3	.722	.3	.356	.3	.670
.4	.689	.4	.781	.4	.430	.4	.763
.5	.736	.5	.840	.5	.505	.5	.856
.6	.782	.6	.899	.6	.580	.6	.950
.7	.829	.7	.959	.7	.655	.7	15.044
.8	.876	.8	9.019	.8	.731	.8	.139
.9	.924	.9	.079	.9	.807	.9	.234
6.0	.971	10.0	.140	14.0	.884	18.0	.330
.1	7.020	.1	.201	.1	.960	.1	.427
.2	.068	.2	.262	.2	12.038	.2	.524
.3	.117	.3	.324	.3	.116	.3	.621
.4	.166	.4	.386	.4	.194	.4	.719
.5	.215	.5	.449	.5	.273	.5	.818
.6	.265	.6	.512	.6	.352	.6	.917
.7	.314	.7	.575	.7	.432	.7	16.017
.8	.365	.8	.639	.8	.512	.8	.117
.9	.415	.9	.703	.9	.593	.9	.218
7.0	.466	11.0	.767	15.0	.674	19.0	.319
.1	.517	.1	.832	.1	.755	.1	.421
.2	.568	.2	.897	.2	.837	.2	.523
.3	.620	.3	.962	.3	.920	.3	.626
.4	.672	.4	10.028	.4	13.003	.4	.730
.5	.725	.5	.095	.5	.086	.5	.834
.6	.777	.6	.161	.6	.170	.6	.939
.7	.830	.7	.228	.7	.254	.7	17.044
.8	.883	.8	.296	.8	.339	.8	.150
.9	.937	.9	.364	.9	.424	.9	.256
8.0	.991	12.0	.432	16.0	.510	20.0	.363
.1	8.045	.1	.501	.1	.596	.1	.471
.2	.100	.2	.570	.2	.683	.2	.579
.3	.155	.3	.639	.3	.770	.3	.638
.4	.210	.4	.709	.4	.858	.4	.797
.5	.266	.5	.780	.5	.946	.5	.907
.6	.321	.6	.850	.6	14.035	.6	18.018
.7	.378	.7	.921	.7	.124	.7	.129
.8	.434	.8	.993	.8	.214	.8	.241
.9	.491	.9	11.065	.9	.304	.9	.353

VAPOUR TENSION OF CAUSTIC POTASH SOLUTIONS FROM 10°—20°.

t	30KOH. 100H$_2$O.	40KOH. 100H$_2$O.	49KOH. 100H$_2$O.
10·0	7·31	6·50	5·62
10·5	7·56	6·72	5·81
11·0	7·82	6·95	6·01
11·7	8·19	7·28	6·29
12·1	8·41	7·47	6·46
12·5	8·63	7·67	6·63
13·0	8·92	7·93	6·86
13·5	9·22	8·19	7·09
13·95	9·49	8·44	7·30
14·5	9·83	8·74	7·56
15·15	10·25	9·11	7·88
15·30	10·35	9·20	7·96
16·0	10·82	9·62	8·33
16·35	11·07	9·85	8·53
17·0.	11·54	10·26	8·88
17·5	11·91	10·59	9·17
18·0	12·29	10·93	9·47
18·5	12·69	11·29	9·78
19·0	13·09	11·65	10·09
19·4	13·41	11·93	10·33
20·0	13·93	12·40	10·75
20·25	14·15	12·59	10·91

II.—Table of Specific Gravity and Percentage of Sulphuric Acid in Aqueous Solution. (Kolbe.)

Sp. gr. at 15° compared with water at 0° = 1.

Degrees Beaumé.	Sp. gr. $d = 15/0.$	100 parts by weight contain H_2SO_4.	Degrees Beaumé.	Sp. gr. $d = 15/0.$	100 parts by weight contain H_2SO_4.
1	1·007	1·9	34	1·308	40·2
2	1·014	2·8	35	1·320	41·6
3	1·022	3·8	36	1·332	43
4	1·029	4·8	37	1·345	44·4
5	1·037	5·8	38	1·357	45·6
6	1·045	6·8	39	1·370	46·9
7	1·052	7·8	40	1·383	48·3
8	1·060	8·8	41	1·397	49·8
9	1·067	9·8	42	1·410	51·2
10	1·075	10·8	43	1·424	52·6
11	1·083	11·9	44	1·438	54·0
12	1·091	13	45	1·453	55·4
13	1·100	14·1	46	1·468	56·9
14	1·108	15·2	47	1·483	58·3
15	1·116	16·2	48	1·498	59·6
16	1·125	17·3	49	1·514	61
17	1·134	18·5	50	1·530	62·5
18	1·142	19·6	51	1·540	64
19	1·152	20·8	52	1·563	65·5
20	1·162	22·1	53	1·580	67
21	1·171	23·3	54	1·597	68·6
22	1·180	24·5	55	1·615	70
23	1·190	25·8	56	1·634	71·6
24	1·200	27·1	57	1·652	73·2
25	1·210	28·4	58	1·671	74·7
26	1·220	29·6	59	1·691	76·4
27	1·231	30·9	60	1·711	78·1
28	1·241	32·2	61	1·732	79·9
29	1·252	33·4	62	1·753	81·7
30	1·263	34·7	63	1·774	84·1
31	1·274	36	64	1·796	86·5
32	1·285	37·4	65	1·81	89·7
33	1·297	38·8	66	1·842	100

II.—TABLE OF SPECIFIC GRAVITY AND PERCENTAGE OF H_2SO_4 IN CONCENTRATED SULPHURIC ACID. (Lunge and Naef.)

Sp. gr. at 15° compared with water at 4° = 1.

Per cent. H_2SO_4.	Sp. gr. $d = 15/4$.	Per cent. H_2SO_4.	Sp. gr. $d = 15/4$
90	1·3185	96	1·8406
91	1·8241	97	1·8410
92	1·8294	98	1·8412
93	1·8339	99	1·8403
94	1·8372	100	1·8384
95	1·8390		

IV.—TABLE OF SPECIFIC GRAVITY AND PERCENTAGE OF NITRIC ACID IN AQUEOUS SOLUTION. (Kolbe.)

Sp. gr. at 15° compared with water at 0° = 1.

Sp. gr. at 15°.	Percentage HNO_3.	Sp. gr. at 15°.	Percentage HNO_3.	Sp. gr. at 15°.	Percentage HNO_3.	Sp. gr. at 15°.	Percentage HNO_3.
1·530	100	1·451	77·6	1·363	58	1·237	37·95
1·529	99·5	1·445	76	1·358	57	1·225	36
1·523	97·9	1·442	75	1·353	56·1	1·218	35
1·516	96	1·438	74	1·346	55	1·211	33·8
1·514	95·2	1·435	73	1·341	54	1·198	32
1·509	94	1·432	72·4	1·339	53·8	1·192	31
1·506	93	1·429	71·2	1·335	53	1·185	30
1·503	92	1·423	69·9	1·331	52·3	1·179	29
1·499	91	1·419	69·2	1·323	51	1·172	28
1·495	90	1·414	68	1·317	49·9	1·166	27
1·494	89·5	1·410	67	1·312	49	1·157	25·7
1·488	88	1·405	66	1·304	48	1·138	23
1·486	87·4	1·400	65	1·298	47·1	1·120	20
1·482	86·1	1·395	64	1·295	46·6	1·105	17·4
1·478	85	1·393	63·6	1·284	45	1·089	15
1·474	84	1·386	62	1·274	43·5	1·077	13
1·470	83	1·381	61·2	1·264	42	1·067	11·4
1·467	82	1·374	60	1·257	41	1·045	7·2
1·463	80·9	1·372	59·6	1·251	40	1·022	4
1·460	80	1·368	58·8	1·244	39	1·010	2
1·456	79						

V.—TABLE OF SPECIFIC GRAVITY AND PERCENTAGE OF HYDROCHLORIC ACID IN AQUEOUS SOLUTION.

Sp. gr. at 15°.	Percentage HCl.	Sp. gr. at 15°.	Percentage HCl.	Sp. gr. at 15°.	Percentage HCl.	Sp. gr. at 15°.	Percentage HCl.
1.007	1.5	1.055	11.0	1.116	23.1	1.175	34.7
1.010	2.2	1.060	12	1.125	24.8	1.180	35.7
1.014	2.9	1.067	13.4	1.134	26.6	1.185	36.8
1.019	3.8	1.075	15	1.143	28.4	1.190	37.9
1.022	4.5	1.083	16.5	1.150	29.7	1.194	38.6
1.029	5.8	1.091	18.1	1.152	30.2	1.199	39.8
1.031	6.2	1.094	18.6	1.159	31.5	1.202	40.5
1.036	7.3	1.100	19.9	1.161	32	1.205	41.2
1.044	8.9	1.105	20.9	1.166	33	1.210	42.4
1.052	10.4	1.108	21.5	1.171	33.9	1.212	43

VI.—TABLE OF SPECIFIC GRAVITY AND PERCENTAGE OF CAUSTIC POTASH IN AQUEOUS SOLUTION.

Sp. gr. at 15°.	Percentage of KOH.	Sp. gr. at 15°.	Percentage of KOH.	Sp. gr. at 15°.	Percentage of KOH.	Sp. gr. at 15°.	Percentage of KOH.
1.009	1	1.166	19	1.374	37	1.590	54
1.017	2	1.177	20	1.387	38	1.604	55
1.025	3	1.188	21	1.400	39	1.618	56
1.033	4	1.198	22	1.412	40	1.630	57
1.041	5	1.209	23	1.425	41	1.642	58
1.049	6	1.220	24	1.438	42	1.655	59
1.058	7	1.230	25	1.450	43	1.667	60
1.065	8	1.241	26	1.462	44	1.681	61
1.074	9	1.252	27	1.475	45	1.695	62
1.083	10	1.264	28	1.488	46	1.705	63
1.092	11	1.276	29	1.499	47	1.718	64
1.101	12	1.288	30	1.511	48	1.729	65
1.110	13	1.300	31	1.525	49	1.740	66
1.119	14	1.311	32	1.539	50	1.754	67
1.128	15	1.324	33	1.552	51	1.768	68
1.137	16	1.336	34	1.565	52	1.780	69
1.146	17	1.349	35	1.578	53	1.790	70
1.155	18	1.361	36				

VII. -Table of Specific Gravity and Percentage of Caustic Soda in Aqueous Solution.

Sp. gr. at 15°	Percentage of NaOH.	Sp. gr. at 15°.	Percentage of NaOH.	Sp. gr. at 15°	Percentage of NaOH.	Sp. gr. at 15°	Percentage of NaOH.
1·012	1	1·213	19	1·405	37	1·580	54
1·023	2	1·225	20	1·415	38	1·591	55
1·035	3	1·236	21	1·426	39	1·601	56
1·048	4	1·247	22	1·437	40	1·611	57
1·058	5	1·258	23	1·447	41	1·622	58
1·070	6	1·269	24	1·457	42	1·633	59
1·081	7	1·279	25	1·468	43	1·643	60
1·092	8	1·290	26	1·478	44	1·654	61
1·103	9	1·300	27	1·488	45	1·666	62
1·115	10	1·310	28	1·499	46	1·674	63
1·126	11	1·321	29	1·509	47	1·684	64
1·137	12	1·332	30	1·519	48	1·695	65
1·148	13	1·343	31	1·529	49	1·705	66
1·159	14	1·353	32	1·540	50	1·715	67
1·170	15	1·363	33	1·550	51	1·726	68
1·181	16	1·374	34	1·560	52	1·737	69
1·192	17	1·384	35	1·570	53	1·748	70
1·202	18	1·395	36				

VIII.—Table of Specific Gravity and Percentage of Ammonia in Aqueous Solution.

Sp. gr. at 14° compared with water at 14° = 1.

Sp. gr.	Percentage of NH₃.	Sp. gr.	Percentage of NH₃.	Sp. gr.	Percentage of NH₃.	Sp. gr.	Percentage of NH₃.
·884	36	·905	27	·931	18	·963	9
·886	35	·907	26	·934	17	·967	8
·888	34	·910	25	·938	16	·970	7
·890	33	·913	24	·941	15	·974	6
·892	32	·916	23	·944	14	·979	5
·895	31	·919	22	·948	13	·983	4
·897	30	·922	21	·952	12	·987	3
·900	29	·925	20	·955	11	·991	2
·902	28	·928	19	·959	10	·995	1

INDEX

THE END

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